

**The Contribution of Biomass Combustion to Ambient Fine Particle
Concentrations in the United States**

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To the memory
of the late
Dr. Glen R. Cass

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Abstract

Biomass combustion is an important source of fine particle emissions to the atmosphere. According to USEPA emissions inventories for the year 1995, approximately 20% of total primary PM_{2.5} emissions come from biomass combustion sources. As an alternative to inventory data such as this, source apportionment with chemical mass balance receptor models can determine the contribution of different fine particle source types to a particular ambient fine particle sample. The identification of individual organic compounds in the fine particle emissions from biomass combustion and other fine particle sources provides a rich source of potential molecular tracers that can be used in apportionment calculations.

A series of experiments were conducted to characterize the fine particle emissions from the following biomass combustion sources: residential wood combustion in fireplaces, non-catalytic wood stoves, and catalytic wood stoves; the prescribed burning of foliar fuels; and the open burning of agricultural waste. Results include emission factors for particle mass, organic and elemental carbon, ionic species, selected elements, and over 200 individual organic compounds as determined by GC/MS analysis. The cellulose pyrolysis product, levoglucosan, was emitted from all of the biomass combustion sources and serves as a unique tracer for biomass combustion in general. Substituted syringols were emitted primarily from hardwood combustion, and resin acids were emitted exclusively from the burning of softwoods. Fine particle emission factors are lower and elemental carbon and PAH emissions are higher from wood stoves than from fireplaces.

The burning of foliar fuels produces more alkanolic acids than wood combustion due to the higher concentration of plant waxes in the foliage.

The data from the residential wood combustion source tests were used in a chemical mass balance receptor model to determine the contribution of biomass combustion to ambient fine particle concentrations throughout the United States. Ambient samples collected as part of the IMPROVE and other sampling networks were combined into seasonal composite samples and analyzed for important molecular markers of biomass combustion and other fine particle sources. The resulting national map provides seasonal and geographical information on the significance of biomass combustion as a fine particle source in the United States.

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Summary

Biomass combustion can be broadly defined as the burning of any biogenic substance excluding fossil fuels and fossil fuel products. Sources of biomass combustion include: energy conversion for cooking and heating; forest brush and weed clearing for land clearing and fire safety; agricultural, municipal and industrial waste incineration; cigarette smoke; charcoal production; structural fires; and wildfires. The particle emissions from biomass combustion can affect the radiative properties of the atmosphere, cloud formation, visibility and public health. Previous studies indicate that the particles emitted from biomass combustion sources are predominantly less than 2 microns in diameter making them susceptible to inhalation and pulmonary deposition. Some of the chemical constituents of the particulate matter emitted from biomass combustion, such as PAH, have potential toxic and/or carcinogenic effects when inhaled by living organisms.

Emissions inventories by the United States Environmental Protection Agency (USEPA) estimate that approximately 20% of the total annual fine particle emissions to the atmosphere come from biomass combustion sources. In some regions and during certain times of the year, this figure can be even higher. If compliance with the recently proposed USEPA fine particle standards is to be attained, biomass combustion must be accurately accounted for in all regional air pollution control strategies. Despite its significance, accurate estimates of biomass combustion emissions remain elusive. The emissions are largely unregulated and arise from diverse area-wide sources. Source-oriented methods to assess the impact of biomass combustion on ambient fine particle concentrations have traditionally combined source test emissions data with land-use, fuel

consumption and industrial or residential activity estimates to calculate pollutant emissions. Atmospheric transport models are then used to predict pollutant concentrations at downwind air sampling sites. However, these methods are limited by often inaccurate inventory estimates, limited data on emission factors, and the short time scales of transport calculations. Alternatively, receptor-based chemical mass balance models, which compare the chemical composition of fine particles emitted from the source to the chemical composition of ambient samples, can resolve the contributions of different source types to a particular ambient sample. While black carbon, water-soluble potassium, and carbon isotope ratios have been used as indicators of biomass combustion, these tracers have other non-biomass sources, and thus are not unique to biomass combustion. The variety and abundance of individual organic compounds emitted from biomass combustion, however, provide a rich source of potential chemical tracers for use in receptor-oriented modeling studies. Some of these organic compounds are not only unique to biomass combustion but also specific to the class or species of plant material being burned.

In order to characterize the emissions from biomass combustion sources, an extensive series of source tests were conducted on the most important source types and fuels found in the United States. Source tests were conducted using an advanced dilution source sampling system designed by Hildemann et al. (1989). Hot exhaust emissions from each source are diluted and cooled with clean particle-free air. Sufficient residence time allows the organic vapors to partition into the particle phase under conditions similar to those experienced in the atmosphere downwind of a source. Particles are then

collected with an array of filter substrates for subsequent chemical analysis, including GC/MS for organic speciation.

The most important biomass combustion source, as determined from inventory estimates, is residential wood combustion. Therefore, the first source considered was the residential combustion of wood in fireplaces. A conventional masonry fireplace was used and exhaust was extracted from the chimney one story above the fire. Wood species selection was based on state level wood fuel consumption activity combined with forestry surveys of the most available woods within each state. Twenty-two wood species were chosen for testing, including 18 of the top 21 most commonly available wood species in the United States. Chapters 1-4 present the results from the fireplace source tests, each chapter representing a region of the U.S. where the wood species considered in that chapter are abundant.

Fine particle mass emission factors from the 22 wood species tested in fireplaces ranged from 1.6 to 11.4 grams per kilogram wood burned. The fine particles consisted primarily of organic compounds, with lesser amounts of elemental carbon, ionic species, and trace elements. Elemental carbon composition of the fine particles varied widely from near 1 to over 30 wt % of the fine particle mass. Softwoods with visually noticeable sap inclusions and woods burned with their bark tended to emit more elemental carbon than the other wood species. The cellulose pyrolysis product, levoglucosan, was the most abundant single organic compound quantified in all of the fireplace source tests. As has been previously determined by other researchers, levoglucosan serves as a unique marker for biomass combustion in general. The emissions of levoglucosan varied from species to species within a general range of 6 - 35% of the total fine particle mass. Substituted

syringols were emitted primarily from hardwood combustion while resin acids were indicative of softwood smoke. Several individual organic compounds were, at least within the current testing program, unique to a particular wood species. Betulin was only found in the emissions from paper birch, juvabione and dehydrojuvabione were unique to balsam fir, friedelin was detected only in the white oak combustion emissions, and yangambin (lirioresinol dimethyl ether) was unique to the yellow poplar. Other potentially significant compounds quantified include retene from the softwoods, β -sitosterol, the amyryns and amyrones, and several tocopherols.

The results from the next biomass source category, residential wood combustion in wood stoves, are given in Chapter 5. The top five available wood species in the U.S. were burned in an iron wood stove and sampling was performed with the same method as the fireplace tests. The wood stove included a catalytic bed designed to reduce pollutant emissions. In order to simulate a wood stove without emissions controls, which is still the most prevalent type in common use in the U.S., the catalytic bed was not engaged for the tests of the five wood species. Two tests were repeated with the catalytic bed in operation to determine its effect on fine particle emissions. Fine particle emission factors were lower from the wood stove combustion of a given wood species than those from fireplace combustion. Elemental carbon composition of the particulate matter is generally higher from the wood stove, and even higher when the catalyst is employed, than that from the fireplace, most likely due to the different combustion conditions. In general the same organic compounds and similar hardwood/softwood distinctions were observed in the wood stove tests as in the fireplace tests. Levoglucosan was still the most abundant organic compound present. PAH emissions were generally higher for the wood

stove tests than for the fireplace tests for the same reason that elemental carbon emissions were enhanced.

Chapter 6 presents the results of the final two biomass combustion source categories considered: the prescribed burning of foliar fuels and the open burning of agricultural waste. These experiments were conducted at a burn chamber at the USEPA research facility in Research Triangle Park, North Carolina. The dilution sampler employed for these tests was based on the Hildemann design with some improvements in automated flow control and data acquisition. Five foliar fuels from throughout the U.S. were selected and tested along with two agricultural waste residues, rice straw and wheat straw. While the fine particle emission factors from these sources were generally higher than the residential wood combustion experiments, the organic compounds detected and quantified were similar. The substituted syringol and resin acid emissions corresponded to the same hardwood/softwood distinction seen in the wood combustion. The agricultural burns produced less substituted guaiacols than the other foliar fuels and less substituted syringols than the hardwood foliage. Another notable difference was the higher emission factors of alkanolic acids and alkanes from the foliar fuel combustion due to the higher abundance of plant waxes in the foliage as opposed to the woody material. Levoglucosan was emitted from both the foliar and agricultural burns at levels comparable to the residential wood combustion tests.

An example of a method for using the source test data of the first five chapters is outlined in Chapter 7. Since many of the source signatures of the fuels tested are not sufficiently unique to resolve each fuel type in a chemical mass balance receptor model, composite residential wood combustion source profiles are calculated on a regional basis.

The procedure is somewhat analogous to deriving fleet average emission profiles for motor vehicles. Wood species availability and wood burning activity are combined on a state by state basis and then emission factors from the source tests are applied according to wood species and appliance type (fireplace vs. wood stove). Particle-phase emissions of relevant organic compounds are then totaled to give regional residential wood combustion source profiles for use in chemical mass balance calculations. The comparison of the regional profiles given in Chapter 7 show that significant differences in source signatures can be expected from region to region. The differences arise largely due to the varying hardwood and softwood availability in different parts of the U.S.

The final chapter gives the results of a chemical mass balance model based on the results of the residential wood combustion source tests. Regional source profiles were calculated as described in Chapter 7 and compared to ambient samples collected as part of the IMPROVE and other national sampling networks. Over 50 sampling sites were examined with the filters from these sites combined into semi-annual seasonal composites prior to chemical analysis. The result of the model calculations is a national map of the contribution of biomass combustion to ambient fine particle concentrations. The cold season showed higher contributions from biomass combustion suggesting that residential wood combustion is a more significant source of fine particles than forest fires. Three other fine particle sources (soil dust, vegetative detritus and motor vehicles) were included in the model with consistent results.

Appendix A gives the complete results of the organic speciation analysis of the ambient samples considered in Chapter 8. Appendix B provides the results of volatile

organic hydrocarbon analysis conducted on the wood stove tests. Appendix C includes results of the gas-phase carbonyl analysis of selected fireplace and wood stove tests.

Chapter 1

Chemical Characterization of Fine Particle Emissions from the Fireplace Combustion of Woods Grown in the Northeastern United States

1.1 Introduction

Fine particle emissions from the fireplace combustion of wood make a significant contribution to ambient fine particle levels in the United States. Emissions inventories compiled by the U.S. Environmental Protection Agency show that in 1995, about 12% of non-fugitive dust fine particle emissions in the United States came from residential wood combustion in fireplaces and wood stoves (1). Other studies show that during winter months, 20-30% of the ambient fine particle mass concentration often can be attributed to wood smoke (2,3), with more than half of the fine particle concentration contributed by wood smoke on some occasions (4). If compliance with the fine particle ambient air quality standards recently promulgated by the USEPA is to be attained, an accurate account of residential wood combustion must be factored into regional air pollution control strategies.

Methods that estimate the contribution of fireplace wood combustion to ambient fine particle levels based on emissions inventory data and atmospheric transport calculations are difficult to apply to specific pollution events that occur on time scales of hours or days. One reason for this is that residential wood burning activity is difficult to predict as behavior varies greatly between households and from day to day. In addition, emissions inventories even under average day conditions are uncertain; emissions factors per kilogram wood burned vary, as will be shown in this paper, by roughly a factor of 5

between different source tests. Additional uncertainties arise from an incomplete knowledge of the amount of wood burned and the type of wood burning appliance used. Alternative source-apportionment techniques, however, do exist that utilize chemical mass balance receptor models (3-5) which compute the best fit linear combination of the chemical species profiles of the primary particle emissions sources in a particular geographic area that is needed to reproduce the chemical composition of ambient fine particle samples. Non-mineral potassium has been suggested as a tracer for wood smoke in receptor models (6). But potassium is also emitted by other major sources such as meat cooking (7) and refuse incineration (8,9) and thus cannot be used as a unique wood smoke tracer in mass balance calculations. Carbon isotope ratios which resolve “contemporary” carbon from “fossil” carbon have also been used as markers for wood combustion (9,10). But “contemporary” carbon has other sources which again include food cooking and refuse incineration as well as the abrasion products from leaf surfaces (11), the natural rubber content of tire dust, and the “contemporary” carbon content of paved road dust.

The wide variety of particle-phase organic compounds emitted from wood combustion provides a rich source of possible chemical tracers for wood smoke which have previously been used in receptor modeling calculations (3,4). Data on the organic speciation of the fine particle emissions from wood combustion have been reported previously (12-15) and significant differences between hardwood and softwood emissions have been found (16-25). However, if these source apportionment methods are to be applied at the national scale, detailed fireplace wood combustion source profiles must be determined for all of the important wood types burned in the United States.

This paper is the first of a series that will present the results from an extensive set of source tests conducted to characterize the particulate organic compound emissions from the fireplace combustion of a wide variety of wood species found in the United States. These results will provide valuable information on the variability in wood smoke tracer emission factors for those organic compounds that are currently used in receptor models and will identify additional tracer compounds that are specific to the smoke from individual wood species. The differences in emissions that occur when different woods are burned can possibly be used to resolve ambient fine particle contributions from combustion of specific wood species and thus, from the specific geographic regions where those species are burned. The present paper documents the organic compound distribution present in the fine particle emissions from important wood species grown in the Northeastern United States.

1.2 Experimental Methods

1.2.1 Wood Selection

Identification of the most common wood species burned in residential fireplaces across the United States was accomplished via a brief review of published data. State-by-state information on residential biomass fuel consumption was taken from U.S. Department of Energy reports (26) and converted to mass of wood burned for residential home heating per state. U.S. Forest Service inventories (27) provided data on the prevalence of specific tree species in existing wood stands in each state. Previous studies have determined that people tend to burn wood that is available in their immediate vicinity (28). By apportioning statewide residential wood fuel consumption in proportion

to the tree species distribution within the state, and then summing the results over the entire United States, a national ranking of the most commonly available wood species for residential combustion was achieved. Table 1.1 lists the top 21 wood species ordered by an index equal to 100 times the nationwide firewood availability for a particular species divided by the total of all firewood availability in the United States. Since we are not at this time attempting to compile a national wood smoke mass emission inventory, we do not need to know the precise amount of each wood burned. Thus, our calculations do not take into account such factors as the general preference for hardwood over softwood, which woods are commercially sold as fuel, regulating agency guidelines on tree clearance, or intrastate population/tree distributions. Our resulting national list and rankings were used as a guide for wood species selection that ensured the inclusion of the most available wood species within our test program. Twenty-two wood species were chosen for testing including 18 of the top 21 most commonly available wood species in the United States; four additional species were chosen in order to address particular issues. Three wood species in the top 21 were not available at the time of testing and are shown in parentheses in Table 1.1. Specimens of the selected woods were then collected from both commercial suppliers and forestry research groups across the U.S. In every case, experts at these facilities provided us with positive species identification.

The 22 woods chosen for testing (Table 1.1) were divided into four groups based on the geographical location in which they grow. Some of the species are found across more than one region. Six wood species found primarily in the Northeastern United States are examined in detail in the present paper and are listed in Table 1.2 along with their scientific names and geographic range over which each is found. Also included is

Table 1.1. Tree species ranked in order of nationwide availability for residential wood burning in the United States. All woods, except those in parentheses, were obtained for our source testing program. Boldface text indicates woods for which source-testing results are presented in this paper that concerns the Northeastern United States; results for all others will be reported in companion papers.

National Rank	Common Name	Scientific Name	Availability Index
1	Red Maple	Acer rubrum	6.7
2	Loblolly Pine	Pinus taeda	5.8
3	Douglas Fir	Pseudotsuga menziesii	4.9
4	White Oak	Quercus alba	4.5
5	Sugar Maple	Acer saccharum	4.2
6	Northern Red Oak	Quercus rubra	4.2
7	Ponderosa Pine	Pinus ponderosa	3.2
8	Yellow Poplar	Liriodendron tulipifera	2.9
9	Black Oak	Quercus velutina	2.8
10	Eastern White Pine	Pinus strobus	2.8
11	White Ash	Fraxinus americana	2.1
12	Sweetgum	Liquidambar styraciflua	2.1
(13)	(White Fir)	(Abies concolor)	(2.0)
14	Quaking Aspen	Populus tremuloides	2.0
(15)	(Shortleaf Pine)	(Pinus echinata)	(1.9)
(16)	(Chestnut Oak)	(Quercus prinus)	(1.9)
17	American Beech	Fagus grandifolia	1.9
18	Eastern Hemlock	Tsuga canadensis	1.9
19	Black Cherry	Prunus serotina	1.8
20	Hickory	Carya sp.	1.7
21	Slash Pine	Pinus elliottii	1.2
36	Paper Birch	Betula papyrifera	0.7
51	Balsam Fir	Abies balsamea	0.5
88	White Spruce	Picea glauca	0.2
139	Pinyon Pine	Pinus edulis	0.1

Table 1.2. Northeastern United States Wood Species Selected for Use in This Study

<u>Tree Species</u>	<u>Scientific Name</u>	<u>Moisture Content of Tested Wood (dry basis)</u>	<u>U.S. Range</u>
Red Maple	<i>Acer rubrum</i>	11%	Entire Eastern U.S.
Northern Red Oak	<i>Quercus rubra</i>	14%	Entire Eastern U.S excluding FL
Eastern White Pine	<i>Pinus strobus</i>	11%	New England south through Appalachians, Northern Midwest
Eastern Hemlock	<i>Tsuga canadensis</i>	30%	Entire Eastern U.S excluding FL
Paper Birch	<i>Betula papyrifera</i>	9%	New England, New York, Northern Midwest
Balsam Fir	<i>Abies balsamea</i>	9%	New England, New York, Northern Midwest

the average moisture content of each wood sample tested, determined by a standard oven-drying method in which one-inch (2.5 cm) thick cross sections from each of two distinct logs were pre-weighed and then baked in an oven at $103^{\circ}\text{C} \pm 2^{\circ}\text{C}$ until no further weight loss occurred (29). The moisture contents of the Northeastern woods tested here ranged from 9% to 30% calculated on a dry basis. Recommended moisture contents for firewood range from 10% to 20%, but the wider range of moisture contents tested here are intended to examine the effect of this parameter on emission factors. The pre-combustion mass and moisture content of the logs to be burned were measured within a few hours before each fireplace test with the moisture content taken to be the average determined from the two samples.

1.2.2 Source Tests

Each wood species was burned in a single test in a conventional masonry fireplace located in a residential building. Logs were cut into pieces of 6-12 inches (15-30 cm) in length with diameters between 3 and 5 inches (7-13 cm). Fires were started with 7-9 pieces of crumpled newspaper and small kindling pieces cut from the same log type being burned. Burn times ranged between 82 and 136 minutes with between 5 and 7 kilograms of wood burned per test. Tests were stopped after the particle sizing instruments showed few particles being emitted; this typically occurred after 10 to 20 minutes of a smoldering fire with no visible flames. Smoke samples were taken from the chimney at a point approximately 4 meters above the fire.

An advanced source sampling system has been developed that facilitates the measurement of fine particle mass emission factors, particle phase organic compounds

and fine particle elemental composition (7, 30). In this dilution source sampler, hot exhaust emissions are mixed with a 20 to 30 fold excess of activated carbon-filtered and HEPA-filtered air which, after sufficient residence time, causes those organic vapors that will form particulate matter upon cooling in the atmosphere downwind of a source to instead condense onto pre-existing particles in the source exhaust within the dilution sampler itself. The emissions thus can be sampled at near atmospheric temperature and pressure in order to obtain an accurate representation of the partitioning of organic compounds

between the gas and particle phases. A dilution ratio of 20 to 30 was chosen to ensure that sufficient organic mass was collected for organic speciation analysis. Previous characterizations of this sampling system (30) suggest that use of dilution ratios higher than 30 would not cause less organic vapor condensation onto existing particles and thus our dilution ratio is sufficient to achieve accurate gas/particle partitioning.

The samples are withdrawn from the dilution source sampler through AIHL-design cyclone separators (31) which are operated at a nominal flow such that fine particles with aerodynamic diameters smaller than $2.5\ \mu\text{m}$ pass through the cyclones along with all gas-phase species. Fine particles are collected with a series of six sampling trains that operate in parallel, each with its own cyclone separator. In the first sampling train, after passing through the cyclone separator, the flow is divided between three filter assemblies. The first contains two quartz fiber filters (47 mm diameter, Pallflex tissue quartz 2500 QAO) operated in series at a nominal flow rate of 5 lpm. These filters are intended for subsequent analysis for organic carbon (OC) and elemental carbon (EC) (32) with the back-up filter providing information on the organic vapor adsorption artifact.

The second filter assembly, operated at a nominal flow rate of 1 lpm, contains a Teflon filter which is used for gravimetric mass determination as well as ion chromatography (IC) (33) or X-ray fluorescence (XRF) analysis (34). The third filter assembly, operated at a nominal flow rate of 15 lpm contains an additional Teflon filter also used for gravimetric mass, IC and XRF analyses as needed.

The second sampling train contains an AIHL-design cyclone separator followed by two identical filter assemblies in parallel each consisting of a single quartz fiber filter operated at a nominal flow rate of 10 lpm. The fine particle phase emissions collected by the quartz fiber filter are subjected to detailed organics analysis by gas chromatography/mass spectrometry (GC/MS). The third cyclone separator is followed by two identical filter assemblies each consisting of a quartz fiber filter followed by a back-up quartz fiber filter. The back-up quartz filters can be analyzed to determine which organic gases are adsorbed onto the filters. The remaining three cyclone separators each are followed by two single quartz fiber filters operated in parallel intended to collect additional organic particulate matter mass that may be needed for GC/MS analysis.

Electronic particle sizing instruments also were connected to the residence time chamber of the dilution source sampler during the fireplace source tests in order to obtain particle size distribution measurements. This instrumentation includes a differential mobility analyzer (TSI model 3071) with a TSI model 3760 condensation nuclei counter and a PMS-ASASP-X 32 channel laser optical particle counter, all operated downstream of a 12 liter secondary dilution chamber in which particle concentrations are reduced by mixing with bottled zero air.

1.2.3 Organic Chemical Analyses

Extraction of particle phase organic compounds collected on quartz fiber filters during the source tests follows the procedures established previously by Mazurek et al. (35) and Rogge et al. (36). Prior to sampling, the quartz fiber filters are baked at 550°C for a minimum of 12 hours to reduce residual carbon levels associated with new filters. Immediately after sampling, the filters are stored in a freezer at -21°C until the samples are extracted. Before the quartz fiber filters are extracted, they are spiked with a mix of deuterated internal recovery standards including four deuterated polycyclic aromatic hydrocarbons (PAH), four deuterated alkanes, and three deuterated alkanolic acids all spanning a wide range of GC retention times. The samples are extracted twice with hexane (Fischer Optima Grade), followed by three successive benzene/isopropanol (2:1) extractions (benzene: E&M Scientific; isopropanol: Burdick & Jackson). The benzene is re-distilled prior to use in order to reduce impurity levels. Extracts are filtered, combined, and reduced in volume to approximately 1 ml, and are split into two separate fractions. One fraction is then derivatized with diazomethane to convert organic acids to their methyl ester analogs which are more amenable to GC/MS identification and quantification.

Both the derivatized and underivatized sample fractions are analyzed by GC/MS in ion scan mode on a Hewlett-Packard GC/MSD (GC model 6890, MSD model 5973) using a 30 m x 0.25 mm diameter HP-5MS capillary column (Hewlett-Packard). 1-Phenyldodecane is used as a co-injection standard for all sample extracts and standard runs. The deuterated PAH and alkanes in the internal standard are used to determine

extraction recovery for the compounds quantified in the underivatized samples. The deuterated acids in the internal standard are used to determine the extraction recovery in the derivatized fraction and also to verify that the diazomethane reactions are driven to completion.

Although not all organic compounds emitted from air pollution sources are solvent extractable nor are they all elutable from a GC column, hundreds of compounds can be identified and quantified in source emissions. Hundreds of authentic standards have been prepared for the positive identification and quantification of many of the organic compounds found in the current source test program. When quantitative standards cannot be obtained for a given compound or compound class, significant effort is made to obtain a non-quantitative secondary standard that can be used for unique identification of the organic compounds. When a secondary standard is not available, interpretation of mass spectra and mass spectral libraries is used to aid in identification. The method used to quantify a specific compound is indicated in the notes column of Table 1.4 and described in the footnotes of that table. All compounds with an "a" in the notes column were quantified based on an authentic quantitative standard of that compound. A "b" indicates that quantification was based on analogy to quantitative standard compounds from either the same homologous series or with very similar structures and retention times. The remaining compounds, indicated with a "c", were quantified based on the total ion response of authentic standards having similar retention times, functional groups, and degrees of fragmentation. The overwhelming majority of the compounds listed in Table 1.4 also are present in the NIST mass spectral library and their mass spectra including key ions can be viewed there.

1.3 Results

The emission factors for fine particle mass as well as organic and elemental carbon, ionic species and key elements from the fireplace combustion of the Northeastern woods studied are listed in Table 1.3. The fine particle mass emission factors ranged from 2.7 to 11.4 grams per kilogram of wood burned and averaged 5.3 g kg^{-1} over all six wood species tested. This is considerably less than the USEPA emission factor for fireplace wood combustion of 17.3 grams $\text{PM}_{2.5}$ per kilogram wood burned (37) (making the assumption that the particles emitted are predominantly less than 2.5 microns in diameter (38)). However, our results agree with several previous studies of the fine particle emission factors from fireplaces (16, 25, 39-40). There was no observed correlation between wood moisture content and fine particle mass emission factor. The highest fine particle mass emission factor resulted from burning eastern white pine. Several logs of the eastern white pine sample burned were visually observed to include much higher amounts of dried sap than the other woods tested. A visible increase in the amount of smoke produced occurred when these logs were added to the fire. Thus, we believe that the increased emissions were a result of sap inclusions in the wood. Excluding the eastern white pine sample, the average $\text{PM}_{2.5}$ emission factor from the fireplace combustion of the remainder of the Northeastern woods was $4.0 \pm 1.2 \text{ g kg}^{-1}$ wood burned. Average particle size distributions showed little variation from wood to wood with the peak in the volume distribution occurring between 100 and 200 nm. These results are practically identical to the size distribution results displayed in a previous

Table 1.3. Fine Particle Mass Emission Factors and Chemical Composition for the Fireplace Combustion of Selected Northeastern U.S. Wood Species

	<u>Hardwoods</u>			<u>Softwoods</u>	
	Red Maple	N. Red Oak	Paper Birch	E. White Pine	Balsam Fir
Fine Particle Mass (g kg ⁻¹ wood burned)	3.3 ± 0.3	5.7 ± 0.6	2.7 ± 0.3	11.4 ± 2.0	4.8 ± 0.5
Elemental and Organic Carbon (Wt % of Fine Particle Mass)					
Organic Carbon (OC)*	85.5 ± 5.8	87.5 ± 5.4	86.8 ± 6.0	73.4 ± 6.4	106.3 ± 6.5
Elemental Carbon (EC)	6.7 ± 1.9	3.8 ± 0.7	22.0 ± 2.9	31.3 ± 2.8	7.0 ± 0.8
Ionic Species (Wt % of Fine Particle Mass)					
Chloride	0.63 ± 0.03	0.40 ± 0.05	0.65 ± 0.03	0.13 ± 0.01	0.39 ± 0.07
Nitrate	0.60 ± 0.04	0.40 ± 0.07	0.28 ± 0.05	0.17 ± 0.01	0.38 ± 0.10
Sulfate	0.31 ± 0.03	0.42 ± 0.06	1.68 ± 0.05	0.13 ± 0.01	0.33 ± 0.08
Ammonium	0.12 ± 0.02	0.06 ± 0.01	0.21 ± 0.02	0.03 ± 0.01	0.04 ± 0.01
Elemental Species (Wt % of Fine Particle Mass)					
Silicon	0.041 ± 0.005	0.009 ± 0.002	0.137 ± 0.007	0.178 ± 0.003	0.029 ± 0.003
Sulfur	0.127 ± 0.004	0.129 ± 0.002	0.197 ± 0.006	0.080 ± 0.001	0.130 ± 0.003
Chlorine	0.674 ± 0.014	0.357 ± 0.007	0.784 ± 0.016	0.145 ± 0.003	0.488 ± 0.009
Potassium	1.235 ± 0.017	1.001 ± 0.008	0.976 ± 0.018	0.439 ± 0.004	1.324 ± 0.012
Zinc	0.039 ± 0.001	0.012 ± 0.001	0.491 ± 0.008	0.021 ± 0.001	0.073 ± 0.001
Calcium	<0.020	<0.020	<0.020	0.011 ± 0.002	<0.024
Bromine	0.004 ± 0.001	0.005 ± 0.001	0.006 ± 0.001	<0.001	0.002 ± 0.001
Rubidium	0.006 ± 0.001	0.005 ± 0.001	0.006 ± 0.001	0.002 ± 0.001	0.008 ± 0.001
Lead	<0.005	0.003 ± 0.001	0.014 ± 0.002	<0.002	0.004 ± 0.001

*results will include adsorption of gas phase organics onto the quartz-fiber filter which may explain weight percents greater than 100

The following elements were not quantified due to high blank levels: Al, Fe, Cu, Mn, Ni, Ag

The following elements were not found at quantities exceeding detection limits: P, Ti, V, Cr, Co, Ga, As, Se, Sr, Y, Zr, Mo, Pd, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, U

paper by Kleeman et al. (41) where fireplace source tests were conducted using the same sampling equipment and instrumentation.

The results in Table 1.3 also indicate that almost all of the emitted fine particle mass consists of organic compounds. Organic carbon contributes over 80% of the fine particle mass in the emissions from every wood species studied. A true mass balance requires conversion from organic carbon mass to total organic compound mass using a factor that accounts for the hydrogen, oxygen, and sometimes nitrogen and sulfur content of the organic compounds present. This scale factor typically ranges between 1.2 and 1.4 for typical atmospheric samples (42) or higher depending primarily on the oxygen content of the compounds. When such a scale factor is applied to the OC data in Table 1.3, more than 100% of the gravimetric mass of the samples is assigned to measured chemical species. The resulting mass overbalances are most likely caused by organic vapor adsorption onto the quartz fiber filters (43). The organic carbon measured on the back-up filter was less than 20% of that measured on the front filter for all six wood species. Since it is not completely clear whether this represents a positive or negative artifact, the back-up filter data are not used to correct the values measured on the front filter. Instead, the back-up filter data help to establish the range of uncertainties involved. We feel that additional research is needed before a simple correction for organic vapor artifacts can be applied. The elemental carbon content of the fine particle emissions generally ranged between 3 and 7% except that combustion of eastern white pine and paper birch produced much higher EC emissions. The high sap content of the eastern white pine may explain the high elemental carbon emissions since the addition of the sap-coated logs to the fire produced a thick visible black smoke. The high elemental

carbon emissions from paper birch may be due to the large amount of bark material on the logs which also produced visible black smoke when burned separately.

Potassium is often used as a marker for wood smoke (3,6) and Table 1.3 shows fairly consistent results for potassium emissions across all types of woods tested averaging 1.1 ± 0.4 weight % of the fine particle mass and 4.9 ± 1.5 grams per kilogram wood burned. However, using potassium as a wood smoke marker is confounded by non-wood combustion sources of fine particle potassium such as meat cooking (7).

Better candidates for wood combustion markers can be found in the over 250 organic compounds identified and quantified in the fine particle emissions from the woods burned in this study. Emitted compounds are either volatilized components of the original natural molecules in the wood that recondense into the particle phase or pyrolysis products of the combustion reactions. Table 1.4 lists the detailed organic compound speciation profiles for the six Northeastern wood smokes characterized here, stated in terms of milligrams of each compound per gram of fine particle organic carbon emitted. The data suggest that there are significant differences in the emissions from different wood species. Figures 1.1 and 1.2 illustrate some of these differences through construction of a carbon compound mass balance based on major organic compound classes found in the smokes. The total organic compound mass per sample was estimated as 1.4 times the organic carbon mass per sample; standards for the individual compounds were used to compute the quantities of each specific compound and the individual compounds were summed to arrive at the overall contribution of each compound class.

Between 17% and 32% of the total organic compound mass emitted from each of the six woods was identified and quantified. The remaining mass consists of an

Table 1.4. Detailed Speciation of Fine Particle Organic Compounds Emitted from Northeastern U.S. Wood Species (all values expressed as mg g⁻¹ organic carbon (OC) emitted)

Compound	Hardwoods			Softwoods			Notes
	Red Maple	N. Red Oak	Paper Birch	E. White Pine	E. Hemlock	Balsam Fir	
n-Alkanes							
n-heptadecane	-	-	0.052	0.005	-	-	b
n-octadecane	-	-	0.084	0.006	-	-	a
n-nonadecane	+	0.024	0.103	0.021	0.036	0.016	b
n-eicosane	0.084	0.083	0.104	0.026	0.076	0.059	a
n-heneicosane	0.134	0.139	0.103	0.027	0.085	0.110	b
n-docosane	+	0.108	+	0.033	0.065	0.141	a
n-tricosane	+	0.118	+	0.047	0.087	0.082	b
n-tetracosane	-	0.041	0.018	0.011	0.043	0.035	a
n-pentacosane	-	0.038	-	-	0.037	0.018	b
n-hexacosane	-	0.009	-	-	0.012	-	b
n-heptacosane	-	-	-	-	0.061	-	b
n-Alkenes							
1-nonadecene	-	-	0.084	0.042	0.024	-	b
1-eicosene	0.229	0.259	0.275	0.087	0.120	0.124	b
1-heneicosene	0.123	0.174	0.185	0.021	0.116	0.359	b
1-docosene	+	0.225	+	0.073	0.124	0.364	b
1-tricosene	0.016	0.149	0.057	-	0.045	0.115	b
1-tetracosene	-	0.122	0.017	0.077	0.164	0.174	b
1-pentacosene	-	0.229	-	0.023	0.047	0.267	b
1-hexacosene	-	0.035	-	0.035	0.063	0.000	b
1-heptacosene	-	0.162	-	0.023	0.222	0.331	b
1-octacosene	-	-	-	-	-	-	b
1-triacontene	-	-	-	-	0.048	-	b
n-Alkanols							
n-octadecanol	-	0.059	-	-	-	-	a
n-nonadecanol	-	0.093	0.034	-	-	0.034	a
n-eicosanol	-	0.286	-	-	-	0.047	a
n-Alkanals							
n-heneicosanal	-	0.071	0.026	-	-	0.032	b
n-docosanal	-	0.121	0.032	-	-	0.076	b
n-tricosanal	-	0.154	0.037	-	-	0.019	b
n-tetracosanal	-	0.081	-	-	0.048	0.060	b
n-pentacosanal	-	0.034	-	-	-	-	b
Alkanoic Acids							
n-decanoic acid	+	+	0.245	0.055	+	+	a,d
n-undecanoic acid	0.036	0.018	0.082	0.015	+	+	b,d
n-dodecanoic acid	+	0.170	0.359	0.074	+	+	a,d
n-tridecanoic acid	0.057	0.042	-	0.022	0.042	0.040	b,d
n-tetradecanoic acid	+	0.243	0.498	0.171	+	0.202	a,d
n-pentadecanoic acid	+	0.163	0.286	0.136	0.240	0.217	b,d
n-hexadecanoic acid	1.830	1.947	2.802	1.636	1.753	1.389	a,d
14-methylhexadecanoic acid	+	+	-	0.182	0.385	0.405	b,d
n-heptadecanoic acid	0.072	0.082	0.151	0.072	0.142	0.121	b,d
n-octadecanoic acid	0.378	0.397	1.434	0.507	0.511	0.402	a,d
16-methyloctadecanoic acid	-	-	-	0.023	0.088	0.060	b,d
n-nonadecanoic acid	0.024	0.061	0.160	0.035	0.086	0.069	b,d
n-eicosanoic acid	0.107	0.253	0.804	0.316	0.665	0.337	a,d
n-heneicosanoic acid	0.074	0.189	0.333	0.034	0.185	0.160	b,d
n-docosanoic acid	0.505	1.236	0.768	0.283	1.540	1.446	a,d
20-methyldocosanoic acid	-	-	-	-	0.013	0.088	b,d
n-tricosanoic acid	0.139	0.347	0.083	0.028	0.209	0.233	b,d

Compound	Hardwoods			Softwoods			Notes
	Red Maple	N. Red Oak	Paper Birch	E. White Pine	E. Hemlock	Balsam Fir	
n-tetracosanoic acid	0.612	4.347	0.166	0.191	4.058	1.526	b,d
n-pentacosanoic acid	0.063	0.200	0.104	0.005	0.131	0.062	b,d
n-hexacosanoic acid	0.073	1.837	0.054	0.016	2.039	0.115	b,d
n-heptacosanoic acid	-	0.108	-	-	0.027	-	b,d
n-octacosanoic acid	-	0.055	-	-	0.256	-	b,d
Alkenoic Acids							
hexadecenoic acid	+	0.074	-	0.051	0.129	0.162	b,d
cis-9-octadecenoic acid	1.108	1.675	-	4.097	1.068	1.298	a,d
trans-9-octadecenoic acid	0.159	0.378	0.164	0.474	0.161	0.257	b,d
2-octadecenoic acid	-	0.055	0.052	-	0.047	0.024	b,d
9,12-octadecadienoic acid	1.217	3.893	1.275	3.840	1.564	1.159	a,d
nonadecenoic acid	-	0.041	-	-	-	-	b,d
eicosenoic acids - 2 isomers	0.153	0.249	0.086	0.137	0.096	0.099	b,d
heneicosenoic acid	-	-	-	-	-	-	b,d
docosenoic acid	0.161	0.241	0.422	-	0.161	0.143	b,d
tricosenoic acid	-	-	-	-	-	-	b,d
tetracosenoic acid	-	0.601	-	-	0.122	0.029	b,d
pentacosenoic acid	-	0.196	-	-	-	-	b,d
hexacosenoic acid	-	0.123	-	-	-	-	b,d
Alkanedioic Acids							
hexanedioic acid	0.265	0.132	0.258	0.095	0.132	0.118	a,d
heptanedioic acid	0.084	0.076	-	0.042	0.058	0.042	a,d
octanedioic acid	0.116	0.122	0.162	0.071	0.085	0.095	a,d
nonanedioic acid	+	0.336	0.224	0.114	0.199	0.149	b,d
decanedioic acid	-	0.065	0.107	0.021	0.026	0.047	a,d
undecanedioic acid	-	-	-	-	-	-	b,d
hexadecanedioic acid	0.103	0.112	0.101	0.052	0.830	0.645	b,d
octadecanedioic acid	-	0.067	0.070	-	0.194	0.109	b,d
eicosanedioic acid	-	0.065	0.069	0.023	0.137	0.171	b,d
docosanedioic acid	0.100	0.086	0.488	-	0.153	0.182	b,d
tetracosanedioic acid	-	0.320	-	-	0.031	-	b,d
pentacosanedioic acid	-	0.118	-	-	-	-	b,d
hexacosanedioic acid	-	0.070	-	-	-	-	b,d
Methyl Alkanoates							
methyl hexadecanoate	0.106	0.123	0.082	0.038	0.095	0.076	a
methyl 14-methylhexadecanoate	-	-	-	0.007	-	0.056	b
methyl heptadecanoate	-	0.013	0.010	-	-	0.016	b
methyl octadecanoate	0.015	0.016	0.039	0.022	0.028	0.024	a
methyl eicosanoate	-	0.010	0.019	0.019	0.017	0.017	b
methyl heneicosanoate	-	-	0.004	-	-	0.007	b
methyl docosanoate	-	0.056	0.005	0.009	0.038	0.094	b
methyl tricosanoate	-	-	0.005	-	-	0.017	b
methyl tetracosanoate	-	0.066	0.008	0.010	0.127	0.103	b
methyl pentacosanoate	-	-	-	-	-	0.015	b
methyl hexacosanoate	-	0.016	-	-	0.040	0.014	b
Ethyl Alkanoates							
ethyl tetracosanoate	-	-	-	-	0.192	-	b
ethyl hexacosanoate	-	-	-	-	0.129	-	b
Methyl Alkenoates							
methyl cis-9-octadecenoate	-	-	0.048	0.101	0.061	0.066	a
methyl 9,12-octadecadienoate	-	0.045	0.105	0.125	0.045	0.368	b
methyl docosenoate	-	-	-	-	-	0.014	b
methyl tetracosenoate	-	-	-	-	-	0.011	b
Guaiacol and Substituted Guaiacols							
guaiacol	-	0.190	0.136	0.074	0.184	0.356	a
eugenol	0.066	0.059	0.174	0.075	0.161	0.254	a

Compound	Hardwoods			Softwoods			Notes
	Red Maple	N. Red Oak	Paper Birch	E. White Pine	E. Hemlock	Balsam Fir	
cis-isoeugenol	0.021	0.041	0.061	0.083	0.124	0.195	a
trans-isoeugenol	0.137	0.268	0.608	0.678	1.299	1.382	b
4-vinylguaiaicol	0.252	0.190	0.134	0.123	0.251	0.428	b
4-ethylguaiaicol	0.028	0.050	0.049	0.049	0.090	0.203	a
4-propylguaiaicol	-	0.017	0.026	0.048	0.068	0.121	a
vanillic acid	0.252	3.787	0.335	0.482	1.629	2.997	a
methyl vanillate	+	0.072	0.154	0.165	0.231	0.237	a
homovanillic acid	2.474	11.072	1.016	2.889	18.139	24.111	a
methyl homovanillate	0.071	0.122	0.047	0.064	0.173	0.210	a
vanillin	+	2.050	7.205	5.164	5.088	5.710	a
acetovanillone	1.624	2.357	3.395	2.988	5.425	5.967	a
propiovanillone	0.533	1.187	0.584	0.939	2.746	2.960	b
guaiaicyl acetone	4.352	7.240	4.644	4.436	16.280	17.678	b
coniferyl aldehyde	13.724	17.271	6.631	7.374	39.003	30.954	a
Syringol and Substituted Syringols							
syringol	0.700	2.588	15.354	+	+	0.258	a
4-ethylsyringol	2.777	2.821	10.106	0.132	-	0.335	b
4-propylsyringol	2.397	1.816	2.034	0.054	-	0.176	b
methoxyeugenol	5.830	3.035	6.632	0.166	0.100	0.607	b
cis-methoxy-isoeugenol	0.786	1.367	0.485	0.125	0.449	0.344	b
trans-methoxy-A113isoeugenol	3.121	2.578	0.859	0.024	0.165	0.653	b
syringic acid	-	4.930	-	-	-	-	a
syringaldehyde	27.022	21.967	13.800	2.355	3.609	7.446	a
acetosyringone	7.209	9.905	2.979	0.576	1.021	3.122	a
syringyl acetone	19.510	28.593	7.474	1.025	1.773	7.184	b
propionyl syringol	1.582	2.109	0.746	0.167	0.267	0.588	b
sinapyl aldehyde	7.496	8.224	5.987	0.219	-	1.088	a
Other Substituted Benzenes and Phenols							
1,2-benzenediol (pyrocatechol)	0.799	5.434	1.110	1.512	0.952	7.114	b
1,4-benzenediol (hydroquinone)	0.625	5.570	0.919	0.356	1.146	4.793	a
1,3-benzenediol (resorcinol)	0.699	2.645	1.326	0.570	0.794	1.134	a
methyl benzenediols	0.345	3.543	0.975	2.395	1.092	7.397	b
methoxybenzenediols	0.281	5.432	1.430	0.088	0.137	1.282	c
hydroxybenzaldehydes	+	0.862	3.423	1.782	1.311	1.518	a
cinnamaldehyde	-	0.903	3.942	3.497	1.662	2.323	b
benzenetriols	-	2.057	-	-	-	0.324	b
hydroxyacetophenones	0.205	0.706	0.634	0.501	0.726	1.018	b
methyl hydroxybenzoates	+	0.198	0.262	0.083	0.129	0.176	b
trimethoxybenzenes	2.056	3.844	23.077	0.169	+	0.395	b
3,4,5-trimethoxybenzoic acid	5.786	3.062	0.279	-	0.119	1.446	a
benzoic acid	+	+	0.464	0.185	+	+	a,d
phenyl acetic acid	+	0.055	0.286	0.130	+	0.077	b,d
phenyl propanoic acid	+	+	0.102	0.237	+	+	b,d
Dimers and Lignans							
diguaiacyl ethanes (divanillyls)	0.715	6.562	0.348	3.303	8.788	14.110	b
syringyl guaiacyl ethane	0.297	3.853	0.077	-	-	0.077	b
disyringyl methane	0.072	0.599	0.019	-	-	0.015	b
disyringyl ethane	0.617	8.035	0.213	-	-	0.060	b
shonanin (2-deoxomatairesinol)	0.024	1.069	0.015	0.301	1.377	6.847	c
methyl-2-deoxomatairesinol	-	-	-	-	-	0.154	c
matairesinol	-	0.054	-	-	0.236	0.530	c
conidendrin	-	-	-	-	0.027	-	c
PAH and Alkyl PAH							
phenanthrene	0.087	0.033	0.269	0.157	0.073	0.073	a
anthracene	0.018	0.010	0.050	0.032	0.021	0.021	a
3-methylphenanthrene	+	0.008	0.093	0.063	0.020	0.025	b
2-methylphenanthrene	+	0.014	0.117	0.225	0.028	0.037	b
2-methylantracene	+	0.007	0.061	0.053	0.019	0.023	a

Compound	Hardwoods			Softwoods			Notes
	Red Maple	N. Red Oak	Paper Birch	E. White Pine	E. Hemlock	Balsam Fir	
9-methylphenanthrene	+	0.010	0.126	0.096	0.024	0.029	b
1-methylphenanthrene	+	0.013	0.111	0.498	0.022	0.047	a
phenylnaphthalenes	+	+	0.266	0.507	0.052	0.107	b
dimethyl or ethyl 178 MW PAHs	+	+	0.087	1.196	0.103	0.122	a
fluoranthene	0.315	0.183	1.083	1.040	0.372	0.286	a
acephenanthrylene	0.117	0.106	0.421	0.500	0.212	0.162	b
pyrene	0.423	0.224	1.080	0.896	0.401	0.310	a
methyl 202 MW PAHs	0.282	0.169	0.299	0.280	0.283	0.235	b
retene	+	+	+	5.485	1.666	0.742	a
benzo[ghi]fluoranthene	0.157	0.059	0.159	0.198	0.129	0.090	b
cyclopenta[cd]pyrene	0.188	0.084	0.235	0.314	0.187	0.122	b
benz[a]anthracene	0.200	0.088	0.213	0.249	0.168	0.127	a
chrysene	0.252	0.107	0.229	0.246	0.176	0.141	a
methyl 226 MW PAHs	0.039	0.018	0.044	0.052	0.035	0.024	b
methyl 228 MW PAHs	0.026	0.026	0.038	0.055	0.028	0.028	b
benzo[b]fluoranthene	0.131	0.036	0.104	0.157	0.066	0.050	a
benzo[k]fluoranthene	0.132	0.048	0.123	0.186	0.084	0.065	a
benzo[j]fluoranthene	0.033	0.022	0.042	0.075	0.038	0.030	b
benzo[e]pyrene	0.079	0.029	0.063	0.078	0.044	0.037	b
benzo[a]pyrene	0.124	0.055	0.127	0.177	0.091	0.070	a
perylene	0.014	0.008	0.013	0.024	0.010	0.009	a
indeno[1,2,3-cd]fluoranthene	0.019	0.010	0.022	0.038	0.017	0.014	b
indeno[1,2,3-cd]pyrene	0.164	0.039	0.108	0.127	0.064	0.053	a
benzo[ghi]perylene	0.066	0.025	0.056	0.070	0.035	0.031	a
anthanthrene	0.012	0.008	0.014	0.023	0.012	0.011	b
dibenz[a,h]anthracene	0.006	0.003	0.005	0.011	0.004	0.005	a
coronene	0.177	0.099	0.156	0.219	0.076	0.099	a
Oxy-PAH							
1,4-naphthalenedione	0.010	0.007	0.036	0.051	0.017	0.016	b
1-naphthol	0.081	0.060	0.204	0.150	0.089	0.128	a
2-naphthol	+	0.135	0.554	0.348	0.217	0.300	a
methylnaphthols	0.242	0.597	0.817	0.699	0.809	1.343	b
methoxynaphthols	0.000	0.074	0.178	0.239	0.212	0.267	a
fluorenone	+	0.046	0.562	0.409	0.127	0.104	a
1-H-phenalen-1-one	0.197	0.287	0.357	0.428	0.506	0.485	a
9,10-anthracenedione	0.117	0.066	0.156	0.136	0.162	0.145	a
xanthone	+	0.040	0.057	0.028	0.072	0.059	a
benzanthrone	0.086	0.107	0.149	0.250	0.134	0.157	a
Sugar Derivatives							
1,4:3,6-dianhydro- α -D-glucopyranose	+	3.507	11.167	4.037	+	4.720	c
galactosan	-	3.527	-	1.291	2.472	2.582	a
mannosan	3.286	4.745	1.313	9.008	25.571	17.398	a
levoglucosan	108.509	168.254	109.539	52.330	95.450	81.445	a
monomethylinositol	-	0.226	-	0.496	16.758	4.939	c
Coumarins and Flavonoids							
coumarin	0.077	0.049	0.359	0.110	0.080	0.067	a
pinostrobin chalcone	-	-	-	1.168	-	-	b
tetramethoxyisoflavone	0.189	1.099	-	-	-	0.022	b
Furans							
5-hydroxymethyl-2-furaldehyde	-	16.131	14.388	7.665	+	16.901	a
5-acetoxymethyl-2-furaldehyde	0.081	0.211	1.328	0.318	0.267	0.231	a
dibenzofuranols	0.156	0.215	0.174	0.149	0.287	0.330	a
benzonaphthofurans	+	0.163	0.252	0.347	0.321	0.280	c
Resin Acids							
deisopropyldehydroabiatic acid	-	-	-	0.237	0.021	0.113	b,d
16,17-bisnordehydroabiatic acid	-	-	-	0.143	0.003	0.010	b,d
16-nordehydroabiatic acid	-	-	-	0.151	0.016	0.013	b,d

Compound	Hardwoods			Softwoods			Notes
	Red Maple	N. Red Oak	Paper Birch	E. White Pine	E. Hemlock	Balsam Fir	
secodehydroabietic acids	-	-	-	0.549	0.107	0.048	b,d
pimaric acid	-	-	-	0.441	0.107	0.080	a,d
sandaracopimaric acid	-	-	-	1.340	0.170	0.401	b,d
dehydroabietic acid	+	+	-	7.811	1.575	2.316	a,d
8,15-pimaradien-18-oic acid	-	-	-	3.812	0.069	0.116	b,d
isopimaric acid	-	-	-	12.615	0.408	2.000	a,d
levopimaric acid	-	-	-	1.043	0.063	0.770	b,d
abietic acid	-	-	-	20.481	1.983	19.558	a,d
7-oxodehydroabietic acid	-	+	-	0.251	0.051	0.012	b,d
abieta-6,8,11,13-tetraen-18-oic acid	-	-	-	1.988	0.425	0.943	b,d
abieta-8,11,13,15-tetraen-18-oic acid	-	-	-	0.520	0.058	0.204	b,d
abieta-6,8,11,13,15-pentaen-18-oic acid	-	-	-	0.249	0.035	0.198	b,d
neoabietic acid	-	-	-	0.415	-	0.132	b,d
7-oxoabieta-8,11,13,15-tetraen-18-oic acid	-	-	-	0.017	0.005	0.025	b,d
Other Diterpenoids							
18-norisopimara-4(19),7,15-triene	-	-	-	0.024	-	-	b
19-norabieta-8,11,13-triene	-	-	-	0.688	0.010	0.011	b
18-norabieta-8,11,13-triene	-	-	-	0.982	0.018	0.011	a
19-norabieta-4,8,11,13-tetraene	-	-	-	1.043	0.053	0.055	b
18-norabieta-4(19),8,11,13-tetraene	-	-	-	0.439	0.027	0.028	b
dehydroabietane	-	-	-	0.035	0.310	0.012	c
methyl deisopropyldehydroabietate	-	-	-	0.048	0.005	-	c
pimarinal	-	-	-	0.075	0.030	-	c
methyl 8,15-pimaradien-18-oate	-	-	-	0.275	0.051	-	c
methyl isopimarate	-	-	-	0.757	0.132	0.056	a
methyl 16,17-bisnordehydroabietate	-	-	-	0.073	0.016	0.006	c
dehydroabietal	-	-	-	0.075	0.045	0.022	c
methyl 6,8,11,13-abietatetraen-18-oate	-	-	-	0.326	0.115	0.081	c
methyl 8,11,13,15-abietatetraen-18-oate	-	-	-	0.118	0.012	0.021	c
methyl dehydroabietate	-	-	-	1.183	0.342	0.173	a
methyl abietate	-	-	-	0.625	-	-	a
methyl-7-oxodehydroabietate	-	-	-	0.104	0.009	0.043	b
manoyl oxide	-	-	-	0.229	0.039	0.362	c
manool	-	-	-	-	+	5.418	a
juvabione	-	-	-	-	+	15.434	a
todomatuic acid (norjuvabione)	-	-	-	-	-	0.454	b
dehydrojuvabione	-	-	-	-	-	8.133	a
Phytosteroids							
stigmasterol	-	0.429	-	-	-	0.211	a
β-sitosterol	0.793	6.367	0.645	0.305	2.509	4.980	a
stigmast-4-en-3-one (sitostenone)	0.090	0.464	0.096	0.022	0.061	0.150	a
stigmasta-3,5-dien-7-one	-	0.789	0.256	0.055	0.145	0.587	b
stigmasta-4,6-dien-3-one	-	0.258	-	0.028	0.037	0.120	b
stigmastan-3-ol	0.111	0.243	-	-	0.209	0.447	a
stigmastan-3-one	0.065	0.124	0.062	0.012	0.058	0.124	c
Triterpenoids							
allobetul-2-ene	-	-	3.157	-	-	-	c
allobetulone	-	-	0.231	-	-	-	c
allobetulin	-	-	6.362	-	-	-	b
betulin	-	-	46.710	-	-	-	a
β-amyrone	-	0.006	0.051	-	-	-	b
β-amyrin	-	0.019	0.035	-	-	-	a
α-amyrone	-	0.014	0.037	-	-	-	b
α-amyrin	-	0.010	0.019	-	-	-	a
Other Compounds							
1-indanone	0.035	0.043	0.235	0.128	0.096	0.096	a
methyl indanones	-	0.074	0.122	0.178	0.208	0.210	b
squalene	0.076	0.339	0.496	0.114	0.119	0.174	a

Compound	Hardwoods			Softwoods			Notes
	Red Maple	N. Red Oak	Paper Birch	E. White Pine	E. Hemlock	Balsam Fir	
α -tocopherol (vitamin E)	-	0.400	-	-	-	-	a
β -tocopherol	-	0.026	-	-	-	-	b
unresolved complex mixture (UCM)	142	301	194	258	290	399	b

^aIdentification and quantification based on authentic quantitative standard

^bIdentification and quantification based on authentic quantitative standards of compounds with similar structures and retention times

^cIdentification based on relative retention times, mass spectra interpretation, and/or mass spectra libraries, quantification based on TIC response of authentic quantitative standards for other compounds that have similar retention times, functional groups and degree of fragmentation

^dDetected and quantified as methyl ester analog in derivatized fraction

- not detected

+ detected but not quantified due to comparable levels found in blank samples

Figure 1.1. Organic compound mass balance for the fine particle emissions from the fireplace combustion of selected Northeastern U.S. hardwood species

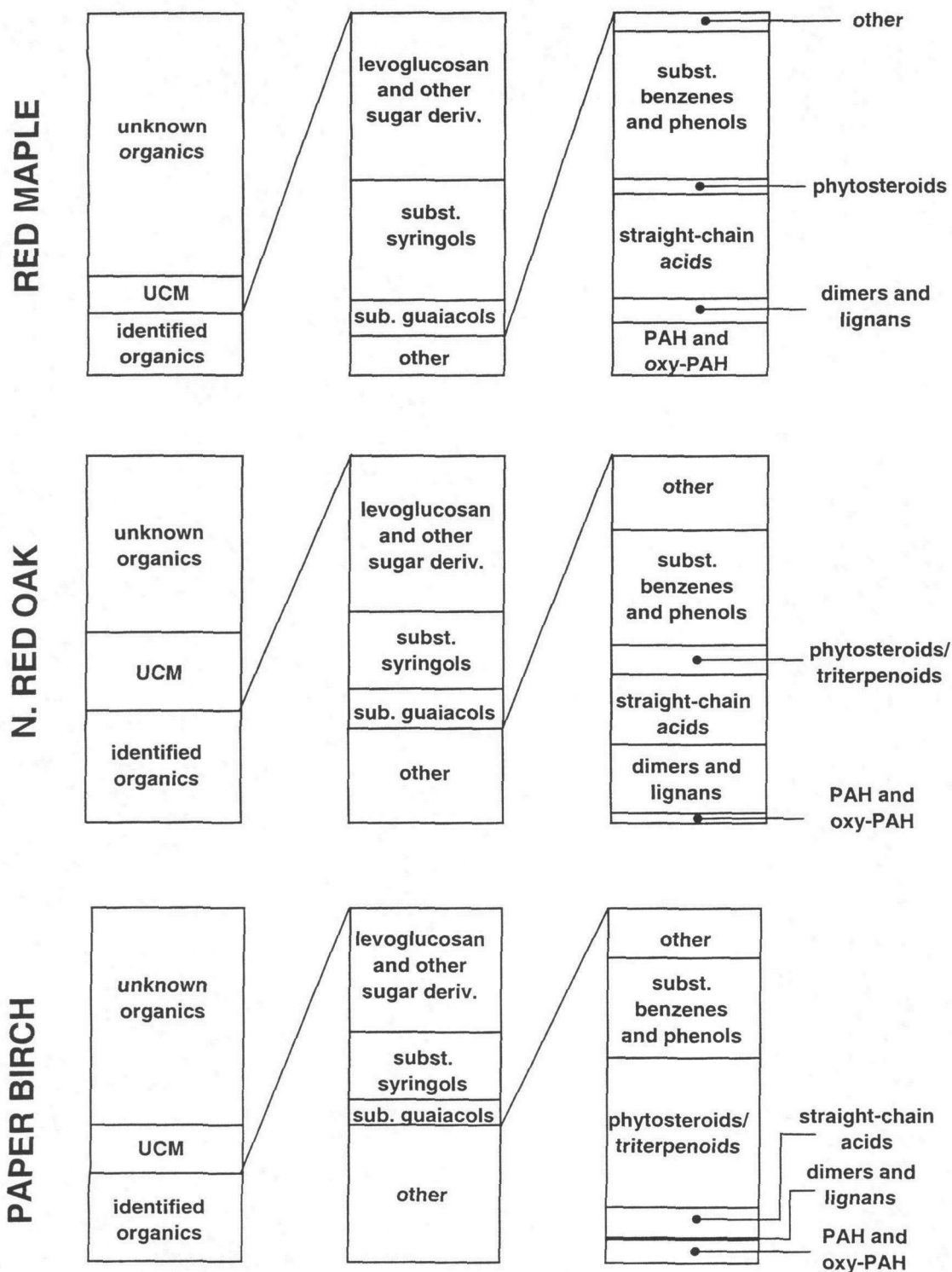
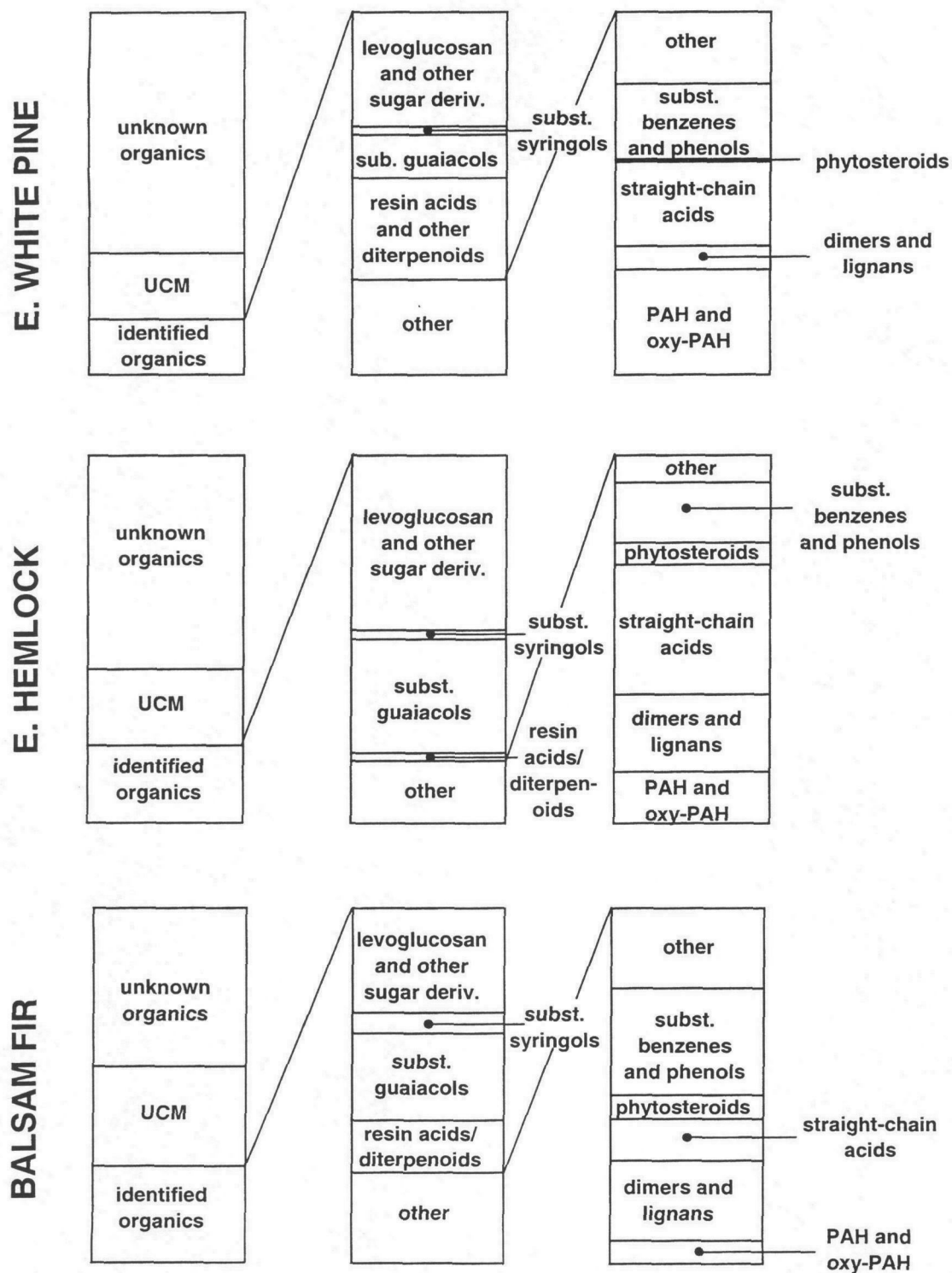


Figure 1.2. Organic compound mass balance for the fine particle emissions from the fireplace combustion of selected Northeastern U.S. softwood species



unresolved complex mixture (UCM) of branched and cyclic organic compounds which passes through the GC column appearing as a hump underlying the resolved peaks, plus an unknown organic fraction that includes compounds that either are not extractable in the organic solvents used here, are not elutable from the GC column, or that remain as unidentified peaks in the gas chromatograms. Of the identified compounds, the pyrolysis product of cellulose, levoglucosan, is by far the most abundant. Between 3% and 12% of the fine particle organic compound emissions are accounted for by levoglucosan, yielding an average of 100 ± 40 mg levoglucosan per gram of fine particle organic carbon emitted. The very high emission factors and uniqueness of this compound to biomass combustion make it an important candidate as a marker for biomass combustion in general as has been proposed previously (44, 45).

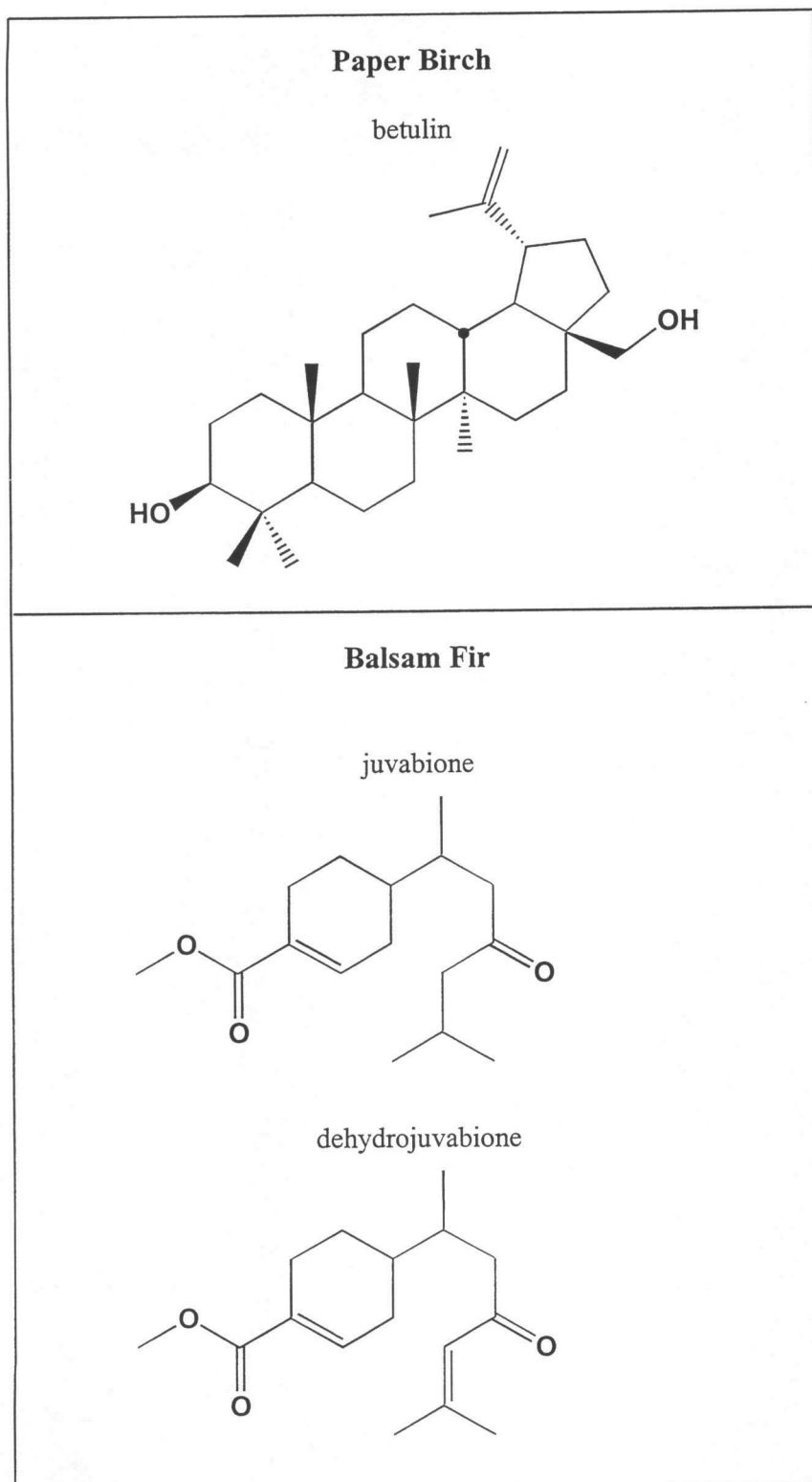
The use of levoglucosan as a long range tracer of biomass combustion depends upon its atmospheric stability which has been explored by Fraser et al. (45). They show that, with respect to the possible reaction mechanism of acid-catalyzed hydrolysis, levoglucosan is stable up to ten days under conditions simulating the aqueous chemistry of atmospheric droplets. The atmospheric reactivity of other potential organic wood smoke tracers is largely unknown. Several PAH listed in Table 1.4 have been shown to degrade in the particle phase when exposed to nitrogen oxides and ozone (46). However, since PAH are only a minor component of wood smoke and are also emitted from a variety of other combustion sources, PAH are not ideal candidates as markers for wood smoke. Although their atmospheric stability has not been tested, many of the substituted guaiacols, syringols, and phenols have been measured in ambient particle samples (3, 4) suggesting they at least do not fully degrade in the atmosphere. If the atmospheric

reaction products of some of these compounds could be identified in ambient samples, they too might be utilized as wood smoke tracers.

A comparison of Figures 1.1 and 1.2 also illustrates the differences in fine particle emissions between hardwoods and softwoods. The hardwood combustion emissions contain greater amounts of substituted syringols than the softwood combustion emissions. Furthermore, resin acids such as dehydroabietic acid and other diterpenoids are significant components of softwood emissions but are not found in detectable quantities in the emissions from hardwoods. Furthermore, while phytosteroids were detected in all of the wood smokes, triterpenoids are not present in any of the softwood smokes. The ability to distinguish between hardwood and softwood smoke using organic chemical tracer techniques has already been demonstrated in California's San Joaquin Valley by Schauer et al. (4). In order to extend that method of analysis to other regions of the United States, both hardwood and softwood source profiles are needed for woods characteristic of the geographical areas of interest. Table 1.4 provides such data for the Northeastern United States.

While organic compound markers for biomass combustion in general and for differentiating between hardwoods and softwoods are known conceptually from previous work, our results are the first to suggest possible organic tracers for the combustion of specific wood species (Figure 1.3). The phytosterol and triterpenoid emissions from burning paper birch illustrated in Figure 1.1 are dominated by emissions of a single triterpenoid, betulin, which is a known component of birch bark (47). About 3% of the total fine particle organic compound mass emitted from paper birch combustion is attributable to betulin. Since betulin was not detected in the emissions from any other

Figure 1.3. Chemical structures of potential species-specific organic tracers for wood smoke



wood species, it appears that betulin and/or its atmospheric transformation products may be a good candidate as a species-specific organic tracer.

Two significant components of the balsam fir combustion emissions, making up over 1.7% of the total fine particle organic compound mass emitted, are juvabione and dehydrojuvabione (also shown in Figure 1.3). These compounds are known components of balsam fir wood (48) which protect the tree from potentially damaging insects by acting as hormone disrupters to insect reproduction (49). While unique to balsam fir emissions, their use as chemical tracers depends upon their atmospheric stability which has not yet been investigated. The presence of several exposed double bonds indicate that these compounds may be subject to ozone attack in the atmosphere. However, the oxidation products of such atmospheric reactions can also be used as molecular tracers for balsam fir combustion, provided that they prove quantifiable in atmospheric fine particle samples.

Besides these compounds that are unique to specific wood species, a closer look at Table 1.4 reveals some important differences in the relative amounts of certain compounds emitted that may be used to distinguish between different wood types. Small amounts of alkanes and alkenes are emitted from the combustion of Northeastern wood species with the peak in the compound distributions occurring generally between carbon numbers 20 and 23. Eastern hemlock combustion emitted measurable levels of heptacosane which was not detected in the other Northeastern woods tested. Small quantities of n-alcohols and n-alkanals were also measured with northern red oak emissions being enriched in n-alkanals in comparison with the other wood species.

Alkanoic acids ranging from carbon numbers 10 to 28 were found in the smoke of the woods tested and exhibit the well-known even carbon number preference for acids found in natural material such as plant epicuticular waxes (50). While all six wood smokes contained high levels of hexadecanoic acid as found in previous wood smoke analyses (25), northern red oak, eastern hemlock, and balsam fir smokes contained tetracosanoic acid as the dominant alkanoic acid. High levels of hexacosanoic acid were also seen in the red oak and eastern hemlock smokes. The dominant alkenoic acids found in all the wood smokes were *cis*-9-octadecenoic acid and 9,12-octadecadienoic acid, although at somewhat different levels. Small amounts of alkanedioic acids as well as methylated or ethylated alkanoic and alkenoic acids were also detected to varying degrees in the emissions from the combustion of the six wood types.

The predominant substituted guaiacols found in the smoke from the six wood species were homovanillic acid, vanillin, acetovanillone, guaiacyl acetone and coniferyl aldehyde. Coniferyl aldehyde was the dominant compound in this class in all wood smokes except for northern red oak which produced higher emissions of vanillin. While both hardwoods and softwoods emitted substituted guaiacols at various levels, the substituted syringols were found to a much greater extent in the hardwood smokes. For the fine particle emissions from red maple and northern red oak combustion, syringaldehyde, acetosyringone, syringyl acetone, and sinapyl aldehyde were the most prevalent substituted syringols. Paper birch smoke also contained high levels of syringol and 4-ethylsyringol in the fine particle emissions. Among other substituted benzenes, trimethoxybenzenes were measured to a much greater extent in the paper birch smoke than in any other wood species. In the balsam fir smoke, divanillyls were the dominant

lignin derived dimers and shonanin (2-deoxomatairesinol) was the dominant lignan. Divanillyls were found in all the other smoke samples but the dimers with at least one syringyl group were found primarily in the hardwood emissions showing the same distinction between hardwood vs. softwood smoke as is the case for the single ring phenolics. A small amount of conidendrin was found only in the fine particle emissions from eastern hemlock.

PAHs are not major contributors to wood smoke mass emissions but many different PAH compounds can be quantified in wood smoke as shown in Table 1.4. Retene was the dominant aromatic hydrocarbon found in the softwood smokes with very little detected in the hardwood combustion emissions. Retene is the fully aromatized thermal alteration product of the resin acids present in conifer woods. Eastern white pine smoke contained considerably higher retene levels than the other two softwood smokes examined here. Other than retene, fluoranthene and pyrene were the most prevalent PAH found in both the hardwood and softwood smoke samples consistent with previous studies of wood smoke where PAH were measured (14, 15). Several oxy-PAH were detected and quantified at low levels and are also listed in Table 1.4.

As discussed above, levoglucosan is the most prevalent sugar derivative emitted from wood combustion. Other sugar derivatives found at lower levels include 1,4:3,6-dianhydro- α -D-glucopyranose, monomethylinositol, galactosan, and mannosan. Eastern hemlock and balsam fir smokes contained higher levels of mannosan and monomethyl inositol than the other wood smokes. Coumarin was found at low levels in all the wood smokes but pinostrobin chalcone was only detected in the eastern white pine. Northern red oak smoke contained higher levels of tetramethoxyisoflavone than the

other wood smokes. The dominant furan emitted was 5-hydroxymethyl-2-furaldehyde found in all the wood smokes except in the red maple smoke and at unquantifiable levels in the eastern hemlock.

Resin acids were only emitted in appreciable quantities in the combustion of the softwoods. Abietic acid was the dominant compound in this class but eastern hemlock smoke contained considerably less abietic acid than the other two softwood smokes. Dehydroabietic acid was the second most abundant resin acid emitted with eastern white pine smoke containing higher levels of dehydroabietic acid than the emissions from the other two softwoods. Other diterpenoids include the methyl esters of the resin acids, diterpenes, as well as juvabione and dehydrojuvabione which are found in the balsam fir emissions, as discussed above. Also prevalent in the balsam fir emissions is manool which was not found at quantifiable levels in any of the other wood smokes discussed here.

β -sitosterol was the most prevalent phytosterol emitted from the combustion of Northeastern woods and was found at very different levels in the different wood smoke types. For instance, the combustion of northern red oak produced almost 20 times more β -sitosterol than eastern white pine as a fraction of the total fine particle organic carbon emitted. Important differences such as this can potentially be used to distinguish between the smokes from the combustion of different wood species.

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Chapter 2

Chemical Characterization of Fine Particle Emissions from the Fireplace Combustion of Woods Grown in the Southern United States

2.1 Introduction

According to U.S. Environmental Protection Agency data for 1995, wood burning in residential fireplaces and wood stoves accounted for 10% of the total fine particle emissions in the Southern United States (1). Within the individual states of North Carolina, Tennessee, and West Virginia, residential wood combustion contributed 18-20% of overall fine particle emissions (1). Such emissions inventory data, however, may be a poor indicator of the wood smoke contribution to ambient fine particle concentrations as wood burning may occur predominantly at night when atmospheric mixing is poor and also may occur in mountain valleys where the terrain can trap emissions. Source-apportionment techniques that utilize chemical mass balance receptor models (2-4) can be used to calculate the contributions from different fine particle sources to ambient fine particle samples even under complex atmospheric transport conditions. Previous suggestions for wood smoke tracers, such as isotopically “contemporary” carbon and non-mineral potassium (5-7), do not act as unique markers for wood smoke since they are also found in the fine particle emissions from meat cooking (8), refuse incineration (6, 9), and the abrasion products from leaf surfaces (10). However, the numerous particle-phase organic compounds that are unique to the emissions from wood combustion do provide better candidate chemical tracers, some of which have been used in receptor modeling calculations previously (2, 3). The particle-phase organic compound emissions from the fireplace combustion of a few wood species

of regional importance have been studied previously (11-20). But in order to apply source apportionment methods based on organic chemical tracers at a national or continental scale, all of the important wood types burned in the United States must be examined

For this reason, an extensive series of source tests was conducted to fully characterize the particulate emissions from the fireplace combustion of the most abundant and available wood species in the United States. This paper presents the results for six wood species found primarily in the Southern United States and is the second of a series of papers (20), each concerning a particular region of the U. S. In addition to determining the species to species variability in the emission factors of the organic wood smoke tracers currently used in receptor-oriented air quality models, this study identifies additional organic compounds that may be specific to the combustion of individual wood species. These species-specific tracers might then be used to determine the region from which particular wood smoke plumes originated based on the geographical range and burning activity of a particular tree species.

2.2 Experimental Methods

2.2.1 Wood Selection

The wood species tested in this study were chosen based on state-level wood burning activity and the abundance of tree species within each state. A previous paper describes the methodology for selecting the most commonly available wood species in the United States (20). Samples of these wood species were supplied by commercial organizations and forestry research groups. Six of these wood species were chosen for

their importance to the Southern U.S region (Table 2.1) and the results from fireplace source tests conducted for these woods are presented here. Table 2.1 also provides the scientific names, geographic ranges, average moisture contents of the woods tested (20), and the national availability ranking (20) of the six Southern U. S. woods.

2.2.2 Source Tests

A previous paper describes the source testing apparatus and procedures used here in detail (20). A residential masonry fireplace was used to burn wood samples of between 5 and 12 kg per test for durations of between 81 and 202 minutes. The smoke was sampled from a port four meters above the fire using the dilution source sampler of Hildemann et al. (8, 20, 21). This sampling apparatus is designed to obtain an accurate representation of the gas/particle partitioning of organic compounds at ambient conditions by diluting the sample with particle-free air and allowing the smoke to cool as organic vapors condense into the particle phase in a residence time chamber. The configuration of the cyclone separators and the filters deployed for fine particle collection is also described in a previous paper (20). Subsequent analyses of the fine particle samples include gravimetric mass, organic carbon (OC) and elemental carbon (EC) (22), ionic species by ion chromatography (IC) (23), elemental composition by X-ray fluorescence (XRF) analysis (24), and organic compound speciation by gas chromatography/mass spectrometry (GC/MS).

Table 2.1. Southern United States Wood Species Selected for Use in This Study

Tree Species	Scientific Name	Moisture Content of Tested Wood (dry basis)	U.S. Range	National Availability Ranking
Loblolly Pine	<i>Pinus taeda</i>	12%	From New Jersey to Texas including entire Southeastern U.S.	2
Yellow Poplar	<i>Liriodendron tulipifera</i>	33%	East Coast from N. Florida to Massachusetts and west to Mississippi River	8
White Ash	<i>Fraxinus americana</i>	11%	Entire Eastern U.S. excluding S. Florida	11
Sweetgum	<i>Liquidambar styraciflua</i>	14%	From New Jersey to Texas including entire Southeastern U.S.	12
Mockernut Hickory	<i>Carya tomentosa</i>	12%	From Massachusetts to Illinois south to E. Texas and east to N. Florida	20
Slash Pine	<i>Pinus elliottii</i>	13%	From W. Louisiana to S. South Carolina south through Florida	21

2.2.3 Organic Chemical Analyses

Organic compound analysis is performed using the methods of Mazurek et al. (25) and Rogge et al. (26) as outlined in a previous paper in this series (20). After the addition of a suite of deuterated compounds for use as internal recovery standards, source samples collected on quartz fiber filters are sonicated in solvent washes twice in hexane (Fischer Optima Grade) and then three times in a 2:1 benzene/isopropanol mixture (benzene: E&M Scientific; isopropanol: Burdick & Jackson). The solvent extracts are then combined and reduced in volume to approximately 1 ml. After splitting the extract into two separate fractions, one portion is derivatized with diazomethane to convert organic acids to their methyl ester analogs which are more amenable to quantification by GC/MS. All GC/MS analysis is performed on a Hewlett-Packard GC/MSD (GC model 6890, MSD model 5973) with a 30 m x 0.25 mm diameter HP-5MS capillary column (Hewlett-Packard). A co-injection standard of 1-phenyldodecane is used to gauge overall instrument response for all injections. Identification and quantification of individual organic compounds is achieved via comparison with a set of prepared authentic standard mixtures containing hundreds of organic compounds found in wood smoke and other source effluents. When a particular standard compound cannot be obtained, identification and quantification are based on similar compounds for which standards are available. Comparison with mass spectral libraries as well as fundamental interpretation of mass spectra are also used to aid in compound identification.

2.3 Results

Table 2.2 lists the emission factors for bulk chemical analysis measured during the fireplace combustion of Southern U.S. woods. Included are data on emissions for fine particle mass, organic and elemental carbon, ionic species and the most abundant chemical elements in the smoke. The fine particle ($d_p < 2.5 \mu\text{m}$) mass emission factor for fireplace combustion of Southern U.S. wood species averaged 4.3 g of particulate matter emitted kg^{-1} of wood burned with a range from 1.6 to 6.8 g kg^{-1} over all six wood species tested. These results correspond well to the 5.3 g kg^{-1} average fine particle mass emission factor from combustion of the Northeastern U. S. woods reported previously (20) and are comparable to several previous studies on fireplace wood combustion (19, 27-29). Our results are significantly less than the present USEPA emission factor for fireplace wood combustion of 17.3 grams $\text{PM}_{2.5}$ per kilogram wood burned (30).

Table 2.2 also indicates that most of the fine particulate mass emitted from the fireplace combustion of the wood species tested is comprised of organic carbon which makes up over 74% of the fine particle mass. In order to convert the mass of organic carbon to an estimate of organic compound mass, it must be multiplied by a scale factor (generally 1.2 to 1.4 for atmospheric samples (31)) to account for the oxygen, hydrogen, and other elemental content of the organic compounds present. In the present study, a scale factor of 1.4 is used owing to the substantial number of oxygenated species in wood smoke. The resulting mass overbalance seen in Table 2.2 for several of the Southern U.S. wood species can most likely be explained by increased organic vapor adsorption onto the quartz fiber filters used for organics collection relative to the Teflon filters from which gravimetric mass measurements were taken (32). The mass overbalance was more

Table 2.2. Fine Particle Mass Emission Factors and Chemical Composition for the Fireplace Combustion of Selected Southern U.S. Wood Species

	<u>Hardwoods</u>				<u>Softwoods</u>	
	Yellow Poplar	White Ash	Sweetgum	Mockernut Hickory	Loblolly Pine	Slash Pine
Fine Particle Mass (g kg ⁻¹ wood burned)	6.8 ± 0.8	3.3 ± 0.3	3.5 ± 0.4	6.8 ± 0.9	3.7 ± 0.4	1.6 ± 0.3
Elemental and Organic Carbon (Wt % of Fine Particle Mass)						
Organic Carbon (OC)*	84.9 ± 5.1	76.8 ± 5.4	78.8 ± 6.0	74.2 ± 6.4	100.4 ± 6.4	100.6 ± 6.5
Elemental Carbon (EC)	3.4 ± 0.4	6.4 ± 0.9	2.7 ± 0.6	1.2 ± 0.2	17.9 ± 1.6	14.2 ± 1.7
Ionic Species (Wt % of Fine Particle Mass)						
Chloride	0.15 ± 0.01	0.46 ± 0.03	0.27 ± 0.03	0.17 ± 0.01	0.26 ± 0.03	0.29 ± 0.05
Nitrate	0.32 ± 0.02	0.65 ± 0.04	0.63 ± 0.04	0.26 ± 0.01	0.26 ± 0.04	0.40 ± 0.07
Sulfate	0.36 ± 0.02	0.77 ± 0.05	0.50 ± 0.04	0.18 ± 0.01	0.19 ± 0.04	1.11 ± 0.08
Ammonium	0.04 ± 0.01	0.07 ± 0.01	0.13 ± 0.01	0.06 ± 0.01	0.08 ± 0.01	0.22 ± 0.03
Elemental Species (Wt % of Fine Particle Mass)						
Silicon	0.019 ± 0.002	0.040 ± 0.004	0.027 ± 0.004	0.008 ± 0.001	0.072 ± 0.004	0.080 ± 0.007
Sulfur	0.101 ± 0.004	0.261 ± 0.010	0.167 ± 0.004	0.081 ± 0.002	0.139 ± 0.003	0.223 ± 0.006
Chlorine	0.124 ± 0.005	0.512 ± 0.013	0.254 ± 0.008	0.164 ± 0.003	0.186 ± 0.007	0.301 ± 0.011
Potassium	0.726 ± 0.006	1.751 ± 0.013	0.797 ± 0.009	0.200 ± 0.003	0.435 ± 0.007	0.653 ± 0.011
Zinc	0.006 ± 0.001	0.049 ± 0.001	0.038 ± 0.001	0.027 ± 0.001	0.037 ± 0.001	0.075 ± 0.002
Calcium	<0.020	<0.030	<0.020	<0.005	<0.020	0.021 ± 0.006
Bromine	<0.001	0.002 ± 0.001	0.002 ± 0.001	0.002 ± 0.0002	<0.003	<0.004
Rubidium	<0.001	0.007 ± 0.001	0.003 ± 0.001	0.001 ± 0.0002	0.002 ± 0.0005	0.007 ± 0.001
Lead	<0.002	0.008 ± 0.002	<0.005	<0.003	<0.004	<0.008

*results will include adsorption of gas phase organics onto the quartz-fiber filter which may explain weight percents greater than 100

The following elements were not quantified because they fell below their respective blank levels: Al, Fe, Cu, Mn, Ni, Ag, P

The following elements were not found at quantities exceeding detection limits: Ti, V, Cr, Co, Ga, As, Se, Sr, Y, Zr, Mo, Pd, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, U

pronounced for the softwood smoke samples suggesting a greater degree of organic vapor adsorption for softwood smoke vs. hardwood smoke as was found in previous Northeastern U. S. wood smoke source tests (20). The elemental carbon content of the fine particle emissions varied widely accounting for between 1 and 18% of fine particle mass, with the softwood smokes containing higher levels of EC than the hardwood smokes, a general trend found previously (29, 33).

While potassium is often used as a marker for wood smoke in general (2, 5), Table 2.2 shows that the potassium emissions from the six wood types tested here range from 0.2 to 1.8 weight % of the fine particle mass. Considering this high degree of variability as well as the existence of other non-wood combustion sources of fine particle potassium (8), its use as a wood smoke tracer may prove problematic.

The more than 250 organic compounds found in the fine particle emissions from the Southern U. S. wood species burned in this study are listed in Table 2.3 along with their emission factors stated in terms of milligrams of each compound per gram of fine particle organic carbon emitted. While many of the compounds are merely volatilized natural products that recondense into the particle phase, others are pyrolysis products of the combustion reactions. The rich variety of organic compounds, along with significant differences in the particulate organic emissions from combustion of different wood species, suggest that these organic markers of wood smoke cannot only be used as tracers for wood smoke in general, but perhaps can help to distinguish between the wood smoke emitted when burning different wood types. Carbon compound mass balances constructed for the emissions from the six wood smokes, based on the major organic compound classes as determined by GC/MS, are given in Figures 2.1 and 2.2. In order to

Table 2.3. Detailed Speciation of Fine Particle Organic Compounds Emitted from Southern U.S. Wood Species (all values expressed as mg g⁻¹ organic carbon (OC) emitted)

Compound	Hardwoods				Softwoods		
	Yellow Poplar	White Ash	Sweet-gum	Mockernut Hickory	Loblolly Pine	Slash Pine	Notes
n-Alkanes							
n-heptadecane	-	0.043	-	-	0.011	-	b
n-octadecane	-	0.034	-	-	0.024	0.030	a
n-nonadecane	0.021	0.070	+	-	0.038	0.038	b
n-eicosane	0.069	0.092	0.056	0.082	0.038	0.056	a
n-heneicosane	0.148	0.170	0.103	0.139	0.054	+	b
n-docosane	0.112	0.137	0.092	0.193	+	+	a
n-tricosane	0.108	0.263	0.099	0.262	+	+	b
n-tetracosane	0.027	0.099	0.030	0.089	0.015	0.032	a
n-pentacosane	0.021	0.203	0.031	0.049	-	-	b
n-hexacosane	-	0.054	0.015	0.012	-	-	b
n-heptacosane	-	0.091	0.026	-	-	-	b
n-octacosane	0.007	0.029	-	-	-	-	a
n-nonacosane	0.018	-	-	-	-	-	b
n-Alkenes							
1-nonadecene	0.029	-	-	-	-	-	b
1-eicosene	0.102	0.329	0.107	0.082	0.027	0.040	b
1-heneicosene	0.157	0.168	0.110	0.131	0.045	0.019	b
1-docosene	0.280	0.238	0.199	0.243	+	+	b
1-tricosene	0.117	0.072	0.095	0.756	0.041	-	b
1-tetracosene	0.046	0.076	0.083	0.244	0.046	0.041	b
1-pentacosene	0.021	-	0.017	0.214	-	-	b
1-hexacosene	-	0.057	0.062	0.105	-	-	b
1-heptacosene	-	-	0.066	0.278	0.046	-	b
1-triacontene	-	-	0.093	-	-	-	b
n-Alkanols							
n-octadecanol	0.063	-	-	0.062	-	-	a
n-nonadecanol	0.044	-	0.041	0.167	-	-	a
n-eicosanol	0.020	-	-	0.116	-	-	a
n-heneicosanol	-	-	-	0.174	-	-	b
n-Alkanals							
n-heneicosanal	0.206	-	-	0.177	-	-	b
n-docosanal	0.265	0.106	0.078	0.398	-	-	b
n-tricosanal	0.221	0.057	0.080	0.405	-	-	b
n-tetracosanal	0.094	-	0.026	0.149	-	-	b
n-pentacosanal	0.023	-	-	0.030	-	-	b
Alkanoic Acids							
n-undecanoic acid	0.016	+	+	0.014	+	+	b,d
n-dodecanoic acid	0.104	0.249	0.249	0.112	+	+	a,d
n-tridecanoic acid	0.050	+	0.058	0.048	0.041	+	b,d
n-tetradecanoic acid	0.194	0.430	+	0.196	+	+	a,d
n-pentadecanoic acid	0.255	+	+	0.151	+	+	b,d
n-hexadecanoic acid	3.297	3.655	1.752	1.971	2.136	+	a,d
14-methylhexadecanoic acid	+	+	+	+	0.201	0.150	b,d
n-heptadecanoic acid	0.201	0.178	0.108	0.194	0.112	+	b,d
n-octadecanoic acid	0.977	1.707	0.446	0.616	0.966	0.661	a,d
16-methyloctadecanoic acid	0.007	-	-	-	0.018	-	b,d
n-nonadecanoic acid	0.127	0.060	0.041	0.148	0.046	0.017	b,d
n-eicosanoic acid	0.542	0.240	0.149	0.311	0.272	0.202	a,d

Compound	Hardwoods				Softwoods		Notes
	Yellow Poplar	White Ash	Sweet-gum	Mockernut Hickory	Loblolly Pine	Slash Pine	
n-heneicosanoic acid	0.216	0.177	0.113	0.401	0.036	+	b,d
n-docosanoic acid	1.190	1.063	0.767	1.463	0.367	0.173	a,d
n-tricosanoic acid	0.474	0.172	0.310	1.092	0.051	0.029	b,d
n-tetracosanoic acid	1.509	1.241	5.322	9.876	0.753	0.542	b,d
n-pentacosanoic acid	0.091	0.066	0.162	0.269	0.012	-	b,d
n-hexacosanoic acid	0.291	0.508	2.470	1.358	0.189	0.262	b,d
n-heptacosanoic acid	0.022	0.030	0.060	0.243	-	-	b,d
n-octacosanoic acid	0.168	0.353	0.091	0.030	-	-	b,d
n-nonacosanoic acid	-	0.030	-	-	-	-	b,d
n-triacontanoic acid	0.175	0.189	-	-	-	-	b,d
Alkenoic Acids							
hexadecenoic acid	0.156	0.152	+	0.208	0.099	+	b,d
cis-9-octadecenoic acid	4.812	1.520	+	1.125	6.253	4.162	a,d
trans-9-octadecenoic acid	1.769	0.409	0.170	0.341	0.347	0.190	b,d
2-octadecenoic acid	-	-	0.058	0.113	-	-	b,d
9,12-octadecadienoic acid	16.440	1.996	1.154	1.597	1.602	1.102	a,d
nonadecenoic acid	-	-	-	0.068	-	-	b,d
eicosenoic acids - 2 isomers	0.203	0.167	0.181	0.412	0.080	0.050	b,d
heneicosenoic acid	-	-	-	0.138	-	-	b,d
docosenoic acid	0.032	-	0.132	0.316	0.019	-	b,d
tricosenoic acid	-	-	0.022	0.095	-	-	b,d
tetracosenoic acid	-	0.089	0.621	5.643	-	-	b,d
pentacosenoic acid	0.048	-	-	0.143	-	-	b,d
hexacosenoic acid	-	-	0.148	0.439	-	-	b,d
Alkanedioic Acids							
hexanedioic acid	0.154	0.257	0.304	0.222	+	+	a,d
heptanedioic acid	0.060	0.126	0.091	0.086	-	+	a,d
octanedioic acid	0.059	0.262	0.165	0.172	0.159	+	a,d
nonanedioic acid	0.108	0.195	0.171	0.263	0.139	+	b,d
decanedioic acid	0.048	0.058	0.042	0.078	0.149	-	a,d
hexadecanedioic acid	0.187	0.116	0.234	0.079	0.113	0.086	b,d
octadecanedioic acid	0.045	-	0.057	0.057	-	-	b,d
eicosanedioic acid	-	-	0.025	0.068	0.050	-	b,d
docosanedioic acid	-	-	0.000	0.067	-	-	b,d
tetracosanedioic acid	-	-	0.059	1.282	-	-	b,d
pentacosanedioic acid	-	-	-	0.222	-	-	b,d
hexacosanedioic acid	-	-	-	0.077	-	-	b,d
Methyl Alkanoates							
methyl hexadecanoate	0.475	0.123	0.078	0.094	0.025	0.040	a
methyl heptadecanoate	0.041	0.013	0.011	0.023	-	-	b
methyl octadecanoate	0.142	0.016	0.021	0.048	0.016	0.024	a
methyl eicosanoate	0.088	0.010	-	0.043	-	-	b
methyl heneicosanoate	0.039	-	-	0.065	-	-	b
methyl docosanoate	0.218	0.056	0.027	0.242	-	-	b
methyl tricosanoate	0.072	-	0.011	0.173	-	-	b
methyl tetracosanoate	0.307	0.066	0.236	0.830	-	-	b
methyl pentacosanoate	0.030	-	-	0.059	-	-	b
methyl hexacosanoate	0.091	0.016	0.114	0.116	-	-	b
methyl heptacosanoate	-	-	-	0.066	-	-	b
methyl octacosanoate	0.024	-	-	-	-	-	b
Methyl Alkenoates							
methyl cis-9-octadecenoate	0.528	-	0.036	0.074	0.071	0.079	a
methyl 9,12-octadecadienoate	1.639	0.045	0.034	0.063	0.045	0.070	b
methyl docosenoate	0.023	-	-	0.055	-	-	b

Compound	Hardwoods				Softwoods		Notes
	Yellow Poplar	White Ash	Sweet-gum	Mockernut Hickory	Loblolly Pine	Slash Pine	
methyl tetracosenoate	0.197	-	-	1.182	-	-	b
methyl hexacosenoate	-	-	-	0.084	-	-	b
Guaiacol and Substituted Guaiacols							
guaiacol	0.194	0.342	0.247	0.211	0.193	0.236	a
eugenol	0.076	0.093	0.081	0.044	0.143	0.161	a
cis-isoeugenol	0.055	0.025	0.015	0.014	0.074	0.069	a
trans-isoeugenol+A156	0.514	0.235	0.130	0.177	0.563	0.605	b
4-vinylguaiacol	0.239	0.312	0.199	0.311	0.108	0.126	b
4-ethylguaiacol	0.052	0.040	0.034	0.038	0.076	0.074	a
4-propylguaiacol	0.015	0.019	0.012	0.014	0.038	0.043	a
vanillic acid	1.659	1.285	1.019	4.009	0.479	0.617	a
methyl vanillate	0.059	+	+	0.202	0.293	0.387	a
homovanillic acid	7.050	4.448	5.059	15.328	5.356	5.990	a
methyl homovanillate	0.101	0.098	0.076	0.267	0.091	0.096	a
vanillin	2.470	2.427	+	2.589	9.712	13.115	a
acetovanillone	1.989	1.959	1.366	3.661	5.652	6.880	a
propiovanillone	0.819	0.799	0.514	1.641	1.422	1.825	b
guaiacyl acetone	5.737	6.164	3.763	9.611	6.362	7.271	b
coniferyl aldehyde	30.048	21.710	17.316	33.243	9.971	10.851	a
Syringol and Substituted Syringols							
syringol	2.779	1.203	1.163	0.828	+	+	a
4-ethylsyringol	3.559	4.278	2.695	5.028	0.509	+	b
4-propylsyringol	2.028	3.613	2.121	4.705	0.223	0.089	b
methoxyeugenol	5.854	6.224	6.746	8.243	0.636	0.244	b
cis-methoxy-isoeugenol	5.027	1.762	2.600	7.841	0.044	-	b
trans-methoxy-isoeugenol	24.890	6.099	8.951	28.048	0.041	-	b
syringic acid	4.351	1.022	2.144	3.061	-	-	a
syringaldehyde	42.042	21.490	36.520	31.774	4.260	3.535	a
acetosyringone	12.800	8.292	13.710	12.431	0.809	0.639	a
syringyl acetone	34.569	25.376	35.057	36.833	1.612	1.056	b
propionyl syringol	3.078	1.599	2.271	2.868	0.267	0.162	b
sinapyl aldehyde	27.514	11.059	20.255	17.245	-	-	a
Other Substituted Benzenes and Phenols							
1,2-benzenediol (pyrocatechol)	4.127	1.741	1.383	9.865	2.600	1.711	b
1,4-benzenediol (hydroquinone)	7.609	1.621	1.435	10.119	0.763	0.295	a
1,3-benzenediol (resorcinol)	2.343	1.225	1.288	3.352	0.661	+	a
methyl benzenediols	4.545	1.040	0.775	12.802	4.006	1.866	b
methoxybenzenediols	5.232	1.011	0.912	5.754	0.231	0.000	c
hydroxybenzaldehydes	1.135	0.493	0.401	1.873	1.338	1.492	a
cinnamaldehyde	0.431	0.355	0.168	0.108	3.789	3.521	b
benzenetriols	2.211	-	-	2.038	-	-	b
hydroxyacetophenones	0.634	0.507	0.461	1.127	0.580	0.703	b
methyl hydroxybenzoates	0.389	0.097	0.063	0.288	0.070	0.080	b
trimethoxybenzenes	4.597	2.638	2.430	3.132	1.036	0.338	b
3,4,5-trimethoxybenzoic acid	8.262	2.110	7.036	6.401	0.174	0.349	a
phenyl acetic acid	0.044	+	+	0.055	0.171	0.228	b,d
phenyl propanoic acid	+	+	+	0.031	0.125	0.166	b,d
Dimers and Lignans							
diguaiacyl ethanes (divanillyls)	3.699	4.327	2.260	7.949	3.012	1.813	b
syringyl guaiacyl ethane	3.242	1.767	1.510	4.063	-	-	b
disyringyl methane	1.024	0.345	0.372	0.616	-	-	b
disyringyl ethane	11.730	2.672	5.580	9.797	-	-	b
shonanin (2-deoxomatairesinol)	0.495	0.209	0.028	0.489	0.500	0.368	c
matairesinol	-	-	-	-	0.056	0.013	c

Compound	Hardwoods				Softwoods		Notes
	Yellow Poplar	White Ash	Sweet-gum	Mockernut Hickory	Loblolly Pine	Slash Pine	
yangambin (lirioresinol dimethyl ether)	2.179	-	-	-	-	-	c
PAH and Alkyl PAH							
phenanthrene	0.035	+	+	0.037	0.400	0.116	a
anthracene	0.007	0.020	0.010	0.008	0.066	0.040	a
3-methylphenanthrene	0.011	-	+	0.021	0.126	0.033	b
2-methylphenanthrene	0.019	0.017	+	0.027	0.338	0.061	b
2-methylantracene	0.011	0.012	0.008	0.021	0.070	0.026	a
9-methylphenanthrene	0.013	-	+	0.022	0.157	0.048	b
1-methylphenanthrene	0.012	+	+	0.011	1.129	0.118	a
phenylnaphthalenes	0.045	+	+	0.050	0.638	0.350	b
dimethyl or ethyl 178 MW PAHs	0.041	+	+	0.074	0.808	0.787	a
fluoranthene	0.253	0.292	+	0.278	0.641	0.868	a
acephenanthrylene	0.139	0.133	0.065	0.134	0.295	0.372	b
pyrene	0.302	0.384	+	0.318	0.595	0.828	a
methyl 202 MW PAHs	1.084	0.972	0.164	0.224	0.225	0.289	b
retene	+	+	+	+	4.533	5.599	a
benzo[ghi]fluoranthene	0.077	0.151	0.085	0.094	0.100	0.131	b
cyclopenta[cd]pyrene	0.124	0.221	0.080	0.162	0.172	0.137	b
benz[a]anthracene	0.123	0.188	0.098	0.140	0.182	0.154	a
chrysene	0.141	0.192	0.120	0.148	0.184	0.192	a
methyl 226 MW PAHs	0.176	0.155	0.022	0.038	0.035	0.035	b
methyl 228 MW PAHs	0.148	0.147	0.020	0.036	0.064	0.025	b
benzo[b]fluoranthene	0.063	0.123	0.070	0.070	0.076	0.099	a
benzo[k]fluoranthene	0.068	0.136	0.066	0.082	0.106	0.085	a
benzo[j]fluoranthene	0.035	0.046	0.021	0.041	0.044	0.031	b
benzo[e]pyrene	0.045	0.078	0.044	0.049	0.057	0.054	b
benzo[a]pyrene	0.085	0.160	0.076	0.102	0.111	0.092	a
perylene	0.010	0.019	0.010	0.013	0.018	0.015	a
indeno[1,2,3-cd]fluoranthene	0.018	0.032	0.012	0.022	0.019	0.025	b
indeno[1,2,3-cd]pyrene	0.060	0.126	0.062	0.067	0.093	0.117	a
benzo[ghi]perylene	0.042	0.075	0.031	0.050	0.045	0.047	a
anthanthrene	0.017	0.020	0.006	0.019	0.009	0.010	b
dibenz[a,h]anthracene	0.005	0.009	0.005	0.007	0.008	0.009	a
coronene	0.160	0.230	0.062	0.173	0.088	0.106	a
Oxy-PAH							
1,4-naphthalenedione	0.011	0.008	0.006	0.017	0.018	0.016	b
1-naphthol	0.110	0.052	0.047	0.332	0.190	0.103	a
2-naphthol	0.206	0.148	0.173	0.693	0.471	0.351	a
methylnaphthols	2.921	3.276	4.281	15.301	3.902	2.922	b
methoxynaphthols	0.090	+	+	0.283	0.337	0.319	a
fluorenone	0.154	+	+	0.185	0.415	0.367	a
1-H-phenalen-1-one	0.474	0.299	0.163	0.379	0.244	0.280	a
9,10-anthracenedione	0.106	0.100	0.104	0.094	0.079	0.143	a
xanthone	0.040	0.043	+	0.061	0.035	0.081	a
benzanthrone	0.164	0.205	0.088	0.173	0.108	0.094	a
Sugar Derivatives							
1,4:3,6-dianhydro- α -D-glucopyranose	2.717	+	+	2.528	6.590	+	c
galactosan	2.925	-	-	3.533	-	-	a
mannosan	14.646	7.683	6.963	6.436	8.024	9.566	a
levoglucosan	156.221	98.973	127.995	159.183	36.373	46.942	a
monomethylinositol	15.764	-	-	-	-	-	c
Coumarins and Flavonoids							
coumarin	0.071	0.090	0.084	0.075	0.123	0.138	a
tetramethoxyisoflavone	1.584	0.749	0.499	1.986	-	-	b

Compound	Hardwoods				Softwoods		Notes
	Yellow Poplar	White Ash	Sweet-gum	Mockernut Hickory	Loblolly Pine	Slash Pine	
Furans							
5-hydroxymethyl-2-furaldehyde	20.193	+	+	11.535	12.921	+	a
5-acetoxymethyl-2-furaldehyde	0.233	0.061	+	0.042	0.428	0.727	a
dibenzofuranols	0.269	0.212	0.175	0.352	0.121	0.094	a
benzonaphthofurans	0.235	+	+	0.249	0.404	0.267	c
Resin Acids							
deisopropyldehydroabietic acid	-	-	-	-	0.302	0.105	b,d
16,17-bisnordehydroabietic acid	-	-	-	-	0.067	0.051	b,d
16-nordehydroabietic acid	-	-	-	-	0.103	0.057	b,d
secodehydroabietic acids	-	-	-	-	0.519	0.150	b,d
pimaric acid	-	-	-	-	2.520	1.365	a,d
sandaracopimaric acid	-	-	-	-	0.464	0.526	b,d
dehydroabietic acid	+	+	+	+	12.329	6.617	a,d
8,15-pimaradien-18-oic acid	-	-	-	-	0.141	0.581	b,d
isopimaric acid	-	-	-	-	0.621	5.818	a,d
levopimaric acid	-	-	-	-	0.682	0.083	b,d
abietic acid	-	-	-	-	29.129	2.643	a,d
7-oxodehydroabietic acid	+	+	+	-	0.337	0.191	b,d
abieta-6,8,11,13-tetraen-18-oic acid	-	-	-	-	2.484	1.885	b,d
abieta-8,11,13,15-tetraen-18-oic acid	-	-	-	-	0.768	-	b,d
abieta-6,8,11,13,15-pentaen-18-oic acid	-	-	-	-	0.268	0.132	b,d
neoabietic acid	-	-	-	-	0.108	-	b,d
7-oxoabieta-8,11,13,15-tetraen-18-oic acid	-	-	-	-	0.027	0.012	b,d
Other Diterpenoids							
18-norisopimara-4(19),7,15-triene	-	-	-	-	0.002	0.009	b
19-norabieta-8,11,13-triene	-	-	-	-	0.386	0.063	b
18-norabieta-8,11,13-triene	-	-	-	-	0.455	0.118	a
19-norabieta-4,8,11,13-tetraene	-	-	-	-	0.566	0.268	b
18-norabieta-4(19),8,11,13-tetraene	-	-	-	-	0.359	0.125	b
dehydroabietane	-	-	-	-	-	0.020	c
methyl deisopropyldehydroabietate	-	-	-	-	0.027	0.025	c
pimarinal	-	-	-	-	0.043	0.094	c
methyl 8,15-pimaradien-18-oate	-	-	-	-	-	0.156	c
methyl isopimarate	-	-	-	-	+	0.312	a
methyl 16,17-bisnordehydroabietate	-	-	-	-	0.013	0.047	c
dehydroabietal	-	-	-	-	+	0.035	c
methyl 6,8,11,13-abietatetraen-18-oate	-	-	-	-	0.169	0.202	c
methyl 8,11,13,15-abietatetraen-18-oate	-	-	-	-	0.086	0.025	c
methyl dehydroabietate	-	-	-	-	0.637	0.618	a
methyl abietate	-	-	-	-	0.145	-	a
methyl-7-oxodehydroabietate	-	-	-	-	0.063	0.033	b
Phytosteroids							
stigmasterol	1.525	0.687	-	0.569	-	-	a
β-sitosterol	2.153	4.256	1.339	3.806	0.271	0.122	a
stigmast-4-en-3-one (sitostenone)	0.162	0.090	0.021	0.508	0.024	0.041	a
stigmasta-3,5-dien-7-one	0.338	0.191	0.128	0.486	-	0.239	b
stigmasta-4,6-dien-3-one	0.182	-	-	0.240	-	-	b
stigmastan-3-ol	0.132	0.170	0.172	0.176	-	-	a
stigmastan-3-one	0.086	-	0.026	0.168	-	-	c
Triterpenoids							
β-amyrone	-	0.103	-	0.164	-	-	b
β-amyrin	-	0.071	-	0.292	-	-	a
α-amyrone	-	0.076	-	0.367	-	-	b

Compound	Hardwoods				Softwoods		Notes
	Yellow Poplar	White Ash	Sweet-gum	Mockernut Hickory	Loblolly Pine	Slash Pine	
α -amyrin	-	0.039	-	0.626	-	-	a
Other Compounds							
1-indanone	0.041	0.040	0.033	0.028	0.091	0.115	a
methyl indanones	0.022	0.030	-	-	0.128	0.132	b
squalene	0.047	0.145	+	0.072	0.083	0.061	a
α -tocopherol (vitamin E)	0.316	-	-	0.127	-	-	a
δ -tocopherol	-	-	-	0.648	-	-	b
β -tocopherol	-	-	-	0.724	-	-	b
unresolved complex mixture (UCM)	415	343	224	501	253	167	b

^aIdentification and quantification based on authentic quantitative standard

^bIdentification and quantification based on authentic quantitative standards of compounds with similar structures and retention times

^cIdentification based on relative retention times, mass spectra interpretation, and/or mass spectra libraries, quantification based on TIC response of authentic quantitative standards for other compounds that have similar retention times, functional groups and degree of fragmentation

^dDetected and quantified as methyl ester analog in derivatized fraction

- not detected

+ detected but not quantified due to comparable levels found in blank samples

calculate an estimated total organic compound mass, organic carbon mass was multiplied by a conversion factor of 1.4. The total mass for each compound class represents the sum of all identified organic compounds within that class.

Of the total organic compound mass emitted from each of the six Southern U.S. woods, between 12% and 40% was quantified as individual organic compounds. In addition, an unresolved complex mixture (UCM) of branched and cyclic organic compounds which appears as an underlying hump in the gas chromatogram was also quantified. The remaining mass consists of an unknown organic fraction which includes unidentified peaks in the gas chromatogram, and compounds that are either not extractable in our organic solvents or are not elutable from the GC column.

Levoglucosan, a pyrolysis product of cellulose, is the most abundant of the identified organic compounds accounting for 3% to 16% of the fine particle organic compound mass emitted. An average of 136 ± 28 mg levoglucosan per gram of fine particle organic carbon was emitted from the combustion of the four Southern hardwood species, while levoglucosan emissions averaged 42 ± 6 mg per gram organic carbon when burning the softwoods studied here. Due to its very high emission factors and its uniqueness to biomass combustion, levoglucosan is an important candidate as a marker for biomass combustion (14, 34).

Clear differences can be seen between the organic compound classes emitted from the combustion of the hardwoods, shown in Figure 2.1, and that of the softwoods, displayed in Figure 2.2. Relatively higher levels of substituted syringols are found in the hardwood smoke while the diterpenoids, including resin acids, are only found at detectable levels in the softwood combustion emissions. These distinctions between the

Figure 2.1. Organic compound mass balance for the fine particle emissions from the fireplace combustion of selected Southern U.S. hardwood species

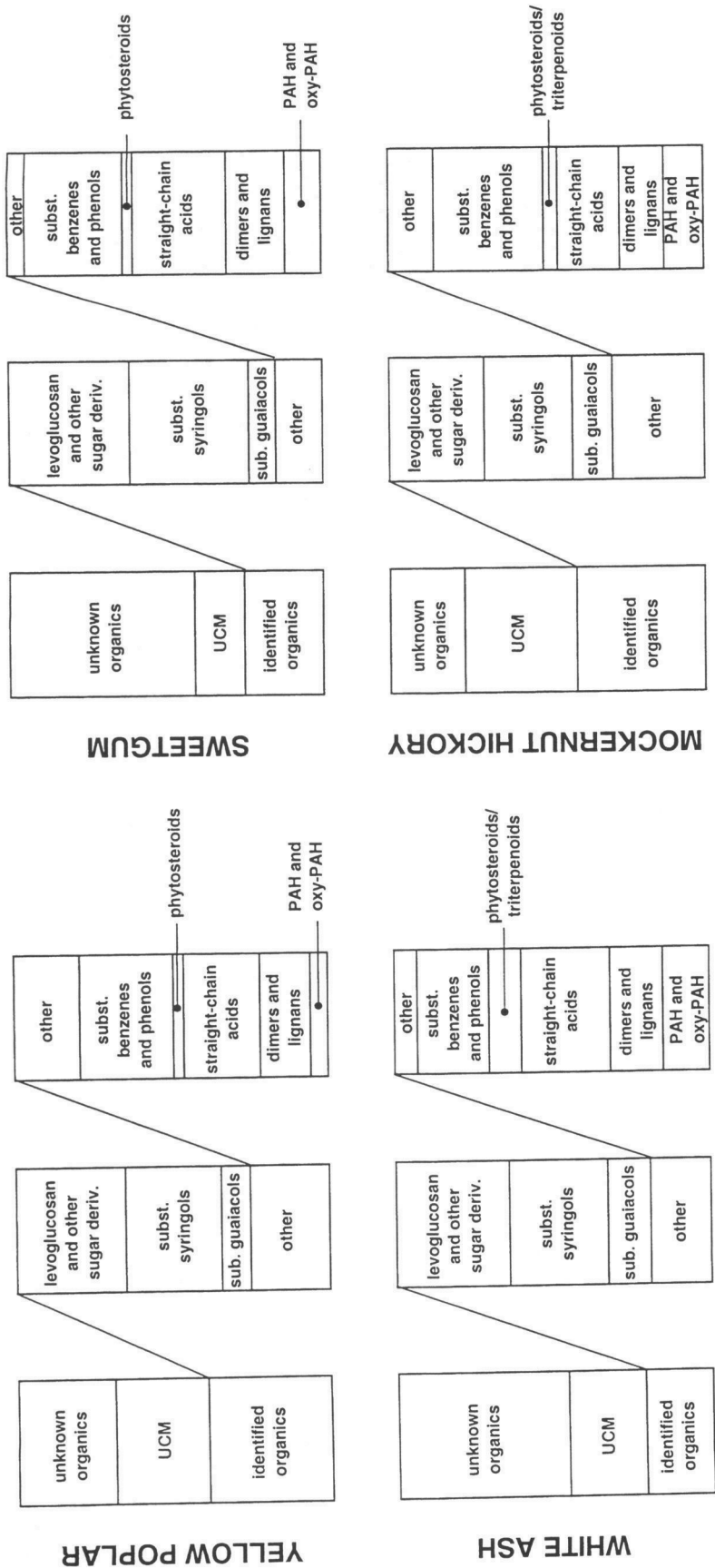
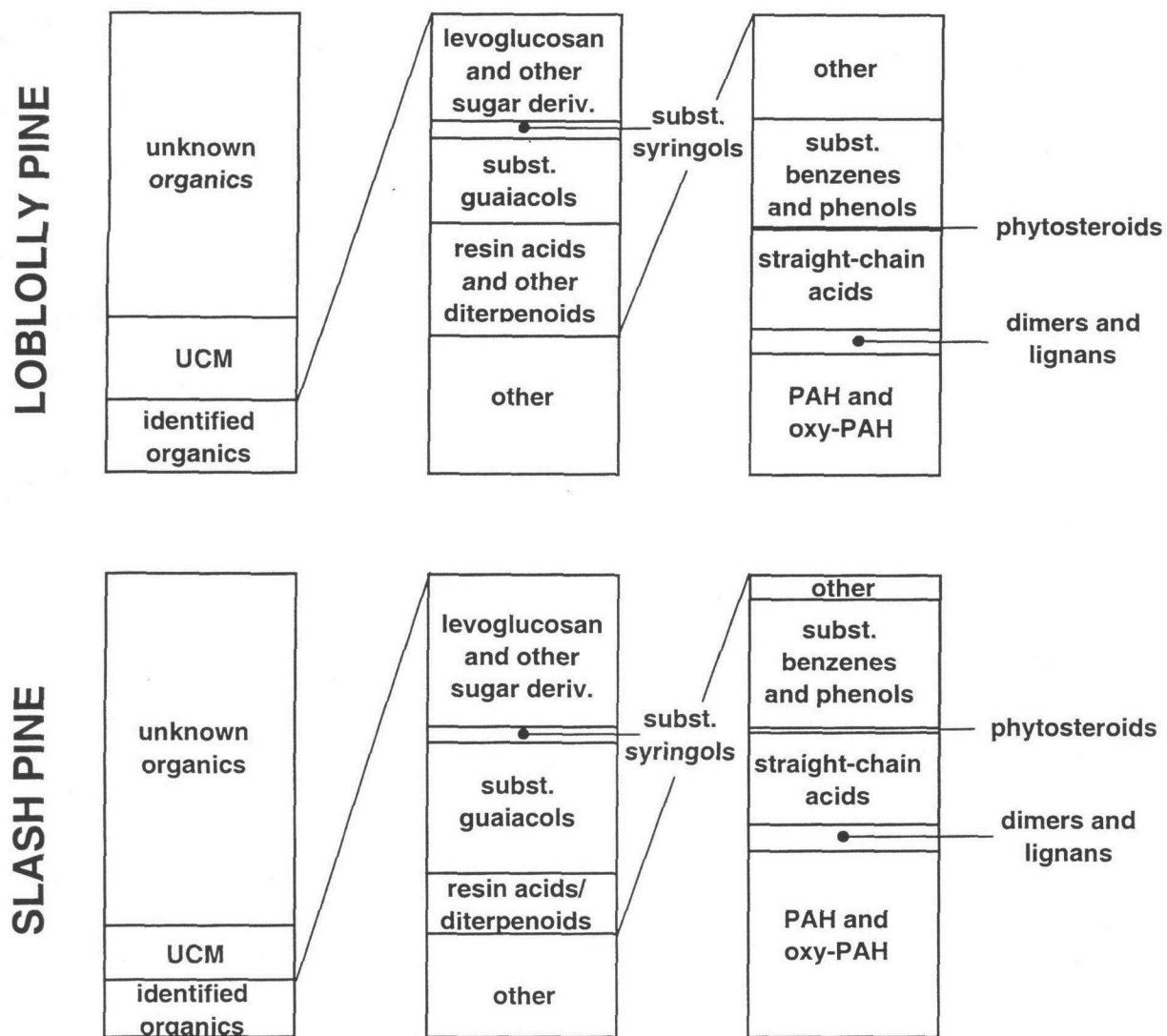


Figure 2.2. Organic compound mass balance for the fine particle emissions from the fireplace combustion of selected Southern U.S. softwood species

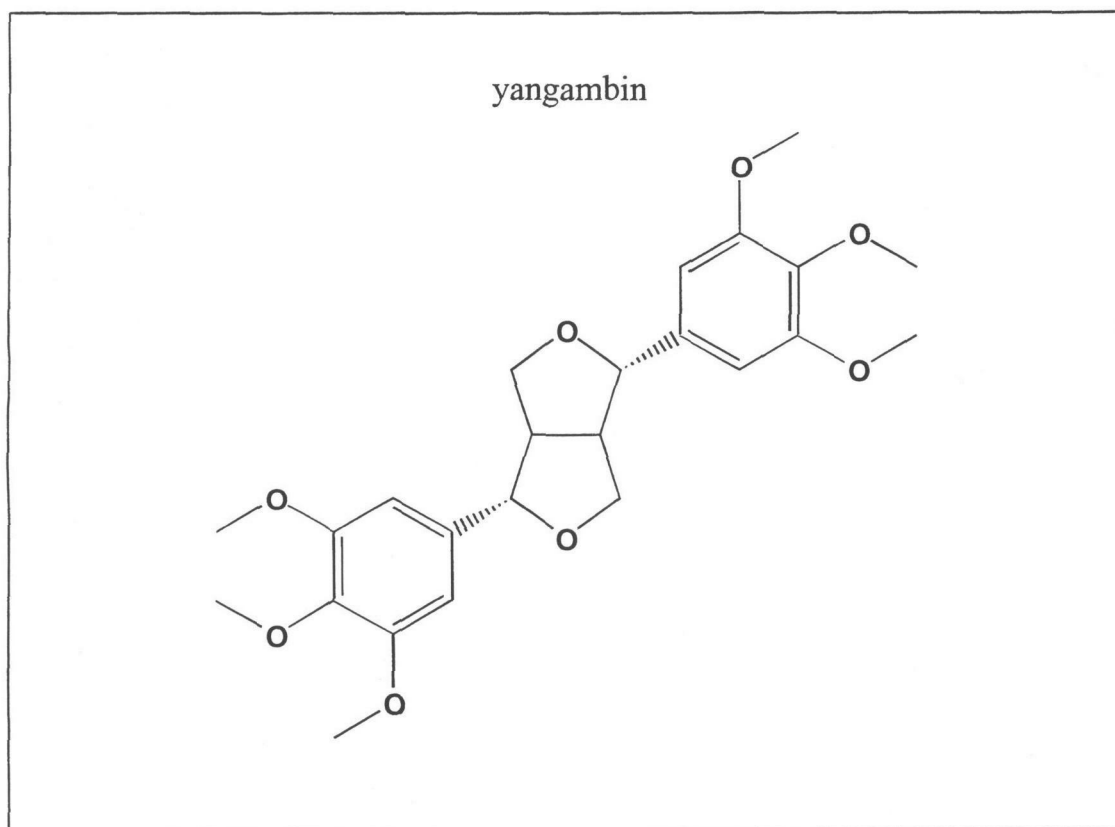


emissions from hardwood and softwood combustion have been used in receptor models to distinguish between hardwood and softwood smokes (3).

Organic compound markers for general biomass combustion, hardwood combustion, and softwood combustion have been proposed and used in previous studies (2, 3). However, our results suggest the existence of organic tracers that are unique to the combustion of specific wood species. Of the 21 wood species from across the United States examined in our national fireplace source testing study, only yellow poplar emitted detectable quantities of the tetrahydrofurofuran lignan known commonly as yangambin (Figure 2.3), which is the dimethyl ether of liriorezinol. Yangambin has been detected in the extracts from the roots and leaves of tree species not found in North America (35-37) but no specific information is available on the yangambin content of yellow poplar. However, another tetrahydrofurofuran, liriodendrin, has been detected in the inner bark of yellow poplar (38). Since a yangambin standard was not available, identification was based on mass spectral libraries while quantification was based on the response of the structurally similar lignan, eudesmin. In the yellow poplar smoke, 2.2 mg of yangambin were emitted per gram of organic carbon. If this compound can be found and quantified in ambient samples, it might prove a useful organic tracer for the combustion of yellow poplar in North America.

Table 2.3 reveals some important differences in the relative amounts of certain compounds emitted that may also be used to distinguish between different wood types. Like the Northeastern wood species results reported previously (20), only small amounts of n-alkanes and n-alkenes are emitted from the combustion of Southern wood species with the peak in the compound distributions occurring generally between carbon numbers

Figure 2.3. Chemical structure of yangambin ($C_{24}H_{30}O_8$, lirioresinol dimethyl ether), a potential species-specific organic tracer for yellow poplar combustion



20 and 23. The two softwoods emitted less n-alkanes and n-alkenes when burned than the four hardwood species. Small quantities of n-alcohols and alkanals were also found but only in the hardwood combustion emissions. Yellow poplar and mockernut hickory smokes contained more n-alkanals relative to the other two hardwood smokes.

Alkanoic acids ranging from carbon numbers 11 to 30 were found in the smoke from the six woods burned exhibiting the well-known even carbon number preference for acids found in natural materials (39) that was also seen in the Northeastern wood species smokes (20). The wood smokes contained high levels of hexadecanoic acid as found in previous wood smoke analyses (19, 20), but sweetgum and mockernut hickory smokes contained relatively high levels of tetracosanoic and hexacosanoic acids compared to the other woods tested. The most abundant alkenoic acids present in all the wood smokes were cis-9-octadecenoic acid and 9,12-octadecadienoic acid, with the exception of mockernut hickory combustion which emitted higher levels of tetracosenoic acid. Yellow poplar smoke contained much higher levels of 9,12-octadecadienoic acid than the other woods. The differences in the carbon number distributions of these straight chain acids, such as the enrichment of C₂₄ acids in mockernut hickory, may prove useful in differentiating between these wood smokes in ambient samples. Small amounts of alkanedioic acids as well as methylated alkanoic and alkenoic acids were also detected in the emissions from the combustion of the six wood types with mockernut hickory smoke exhibiting a C₂₄ acid preference once again.

As was the case with the Northeastern wood smokes (20), the predominant substituted guaiacols found in the smoke from the six Southern wood species were homovanillic acid, vanillin, acetovanillone, guaiacyl acetone and coniferyl aldehyde.

Coniferyl aldehyde was the dominant compound in this class in all wood smokes except for slash pine which produced higher emissions of vanillin. As mentioned above, the substituted syringols were found to a much greater extent in the hardwood smokes but both hardwood and softwood combustion emitted substituted guaiacols at various levels. Syringaldehyde and syringyl acetone were the most prevalent substituted syringols in the Southern U.S. hardwood smokes with trans-methoxy-iso-eugenol, sinapyl aldehyde and acetosyringone also being emitted at high levels. The amounts of cis- and trans-methoxy-iso-eugenol were higher in the yellow poplar and mockernut hickory smokes than in the other hardwoods. These two wood species also show significantly higher emissions of the benzenediols and their substituted analogs than the other wood species tested. Higher levels of trimethoxybenzenes and 3,4,5-trimethoxybenzoic acid were found in the hardwood smokes than in the softwood smokes. In contrast, cinnamaldehyde was more prevalent in the emissions from softwood combustion than in those from hardwood combustion. Divanillyls (14) were found in all the wood smoke samples but the dimers containing the syringyl substitution, as was the case for the single ring substituted syringols, were found primarily in the hardwood emissions.

While PAHs and alkyl PAHs do not constitute a major fraction of the fine particulate mass emitted from fireplace wood combustion, many different PAH compounds were identified and their emission levels and are included in Table 2.3. Similarly to the Northeastern wood smoke samples (20), the most prevalent compound in this class was retene, a fully aromatized thermal alteration product of the resin acids found in conifer wood smoke. As expected, retene was primarily emitted from conifer combustion with very little detected in the hardwood combustion emissions. Table 2.3

also lists several oxy-PAH that were also detected and quantified in the wood smoke samples with methyl naphthols as the predominant oxy-PAH emitted from the combustion of all six Southern U.S. woods.

Levogluconan was already discussed as the most abundant sugar derivative emitted from wood combustion. Other sugar derivatives identified and quantified include 1,4:3,6-dianhydro- α -D-glucopyranose, monomethylinositol, galactosan, and mannosan. Yellow poplar smoke was the only Southern wood species to contain monomethylinositol in measurable quantities but this compound was also found in several of the Northeastern wood smokes (20). The dominant furan emitted, 5-hydroxymethyl-2-furaldehyde, was found at high levels in the smokes from yellow poplar, mockernut hickory, and loblolly pine and was detected but not quantified in the other three wood smokes.

Resin acids were only emitted in appreciable quantities in the combustion of the softwoods with abietic acid and dehydroabietic acid as the most abundant resin acids. Loblolly pine smoke contained significantly more abietic acid than the smoke from slash pine combustion suggesting that the combustion of seemingly similar wood types may result in very different emissions profiles. Other diterpenoids detected in small quantities from softwood combustion include the methyl ester analogs of the resin acids and several diterpenes. β -Sitosterol was the most prevalent phytosterol measured and was found primarily in the hardwood smokes. Since β -sitosterol has been detected in ambient samples as well (34), it may be another good candidate as a wood smoke tracer. Smoke from burning mockernut hickory was the only Southern wood species smoke that

contained β - and δ -tocopherol, although β -tocopherol was also detected in the smoke from northern red oak (20) which also grows in some areas of the Southern U. S.

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Chapter 3

Chemical Characterization of Fine Particle Emissions from the Fireplace Combustion of Woods Grown in the Midwestern United States

3.1 Introduction

Residential wood combustion in fireplaces and wood stoves contributed almost 6% of the fine particle emissions in the Midwestern United States in 1995 (1). In Michigan and Wisconsin, residential wood combustion accounted for 11-13% of fine particle emissions according to estimates provided by the U. S. Environmental Protection Agency (1). Because residential wood burning activity varies greatly between households and from day to day, emissions inventory data are difficult to apply to specific pollution events that occur on time scales of hours or days. Chemical mass balance receptor models (2-4) can be used to determine wood smoke contributions to individual fine particle samples. These models compute the best fit linear combination of the chemical species profiles of the primary particle emission sources in a particular geographic area that is needed to reproduce the chemical composition of ambient fine particle samples. Non-mineral potassium and isotopically “contemporary” carbon have been suggested as tracers for wood smoke in receptor models (5-7). But these potential tracers are also emitted by other major sources such as meat cooking (8), refuse incineration (6, 9), and abrasion products from leaf surfaces (10) and thus cannot be used as unique wood smoke tracers in mass balance calculations.

Unusual organic compounds present in wood can survive the wood combustion process and condense onto the particles in the smoke. These wood smoke markers and

their thermal alteration products act as chemical tracers for wood smoke that can be used in receptor modeling calculations (2, 3). Source tests to determine the organic speciation profiles for the fine particle emissions from fireplace wood combustion have been conducted previously for several wood types (11-20). But in order to apply organic chemical tracer methods to determine wood smoke contributions to atmospheric fine particle concentrations across the United States, fireplace wood combustion source profiles must be determined for all of the most important wood species that are burned nationwide.

This paper, concerning wood species found in the Midwestern United States, is the third of a series (20, 21) that presents the results of source tests conducted to characterize the particulate organic compound emissions from the fireplace combustion of wood. These results are intended for use in chemical mass balance receptor models that seek to identify the wood smoke contribution to ambient fine particle samples. Many of the wood species examined here also grow in the Northeastern U. S. and thus the source profiles developed here have relevance to other regions as well.

3.2 Experimental Methods

3.2.1 Wood Selection

The methods for selecting the wood species tested in this study are described in a previous paper (20). By combining state-level residential wood burning activity (22) and state-level forestry inventories on existing wood stands (23), and by assuming that people burn the wood that is available in their local region (24), a national ranking of the most commonly available wood species for residential combustion was compiled. A previous

paper (20) lists the 21 most available wood species ordered by an index equal to 100 times the nationwide firewood availability for a particular species divided by the total of all firewood availability in the United States. Eighteen of the 21 most commonly available wood species in the United States were chosen for inclusion within our nationwide source test program. Several other wood species were chosen as well in order to examine special issues (e.g., the composition of wood smoke generated indoors on Indian reservations in the case of pinyon pine). Commercial suppliers and forestry research groups provided specimens of these woods along with positive species identification.

The woods chosen for our national source testing program were divided into four groups based on the geographical location in which they grow, although several of the species are found across more than one region. Six wood species found primarily in the Midwestern United States including two oaks, three other hardwoods, and one softwood, are examined in detail in the present paper and are listed in Table 3.1. Table 3.1 also lists the scientific names, geographic ranges, our national availability ranking, and the average moisture content of each wood sample tested determined by a standard oven-drying method described previously (20).

3.2.2 Source Tests

The source testing procedures employed here are described in detail in a companion paper (20). Wood samples were burned in a residential masonry fireplace, and smoke samples were taken from the chimney at a point approximately four meters above the fire. Burn times ranged between 95 and 153 minutes with between 5 and 10

Table 3.1. Midwestern United States Wood Species Selected for Use in This Study

Tree Species	Scientific Name	Moisture Content of Tested Wood (dry basis)	U.S. Range	National Availability Ranking
White Oak	<i>Quercus alba</i>	31%	Entire Eastern U.S. west to S. Minnesota and south to E. Texas	4
Sugar Maple	<i>Acer saccharum</i>	23%	Northeastern and Midwestern U.S. south to Missouri north to Minnesota	5
Black Oak	<i>Quercus velutina</i>	52%	Eastern and Midwestern U.S south to E. Texas and N. Florida	9
American Beech	<i>Fagus grandifolia</i>	13%	Entire Eastern U.S west to Wisconsin and south to Louisiana	17
Black Cherry	<i>Prunus serotina</i>	13%	Entire Eastern U.S west to Minnesota and south to E. Texas	19
White Spruce	<i>Picea glauca</i>	18%	Northern U.S. states from Montana through Michigan to Maine	88

kilograms of wood burned per test. The smoke was sampled with the dilution source sampler of Hildemann et al. (8, 20, 25) that provides sufficient dilution, cooling and residence time to approximate downwind atmospheric conditions in order to obtain an accurate representation of the partitioning of organic compounds between the gas and particle phases. Samples were taken from the residence time chamber of the dilution source sampler through six cyclone separators (26) that removed particles with aerodynamic diameters greater than 2.5 μm . Downstream of the cyclones, fine particle samples were collected on a combination of Teflon and quartz fiber filters which were subsequently analyzed for organic carbon (OC) and elemental carbon (EC) (27), gravimetric mass, ionic species by ion chromatography (IC) (28), elemental composition by X-ray fluorescence (XRF) analysis (29), and speciated organic compounds by gas chromatography/mass spectrometry (GC/MS). The exact configuration of filter media on which fine particles were collected and the analytical methods used are described in detail in a previous paper (20).

3.2.3 Organic Chemical Analyses

The individual organic compounds present in the wood smoke samples were determined using methods established by Mazurek et al. (30) and Rogge et al. (31) as described previously (20). Briefly, the quartz fiber filters are spiked with a mix of deuterated internal recovery standards and then extracted by mild sonication twice in hexane (Fischer Optima Grade) and three times in a benzene/isopropanol mixture (2:1) (benzene: E&M Scientific; isopropanol: Burdick & Jackson). Extracts are filtered, combined, and reduced in volume to approximately 1 ml, and are split into two separate

fractions. One fraction is then derivatized with diazomethane to convert organic acids to their methyl ester analogs. The derivatized and underivatized sample fractions are analyzed by GC/MS on a Hewlett-Packard GC/MSD (GC model 6890, MSD model 5973) using a 30 m x 0.25 mm diameter HP-5MS capillary column (Hewlett-Packard). 1-Phenyldodecane is used as a co-injection standard for all sample extracts and standard runs. Hundreds of authentic standards have been prepared for the positive identification and quantification of many of the organic compounds found in the current source test program. When quantitative standards cannot be obtained for a given compound or compound class, significant effort is made to obtain a non-quantitative secondary standard that can be used for unique identification of the organic compounds. When a secondary standard is not available, interpretation of mass spectra and mass spectral libraries is used to aid in identification. Quantification of compounds identified using secondary standards has been estimated from the response factors for compounds having similar retention times and chemical structure. Estimates of the quantity of a few remaining compounds are based on use of the response factor of compounds with similar polarities, degrees of fragmentation, and retention times.

3.3 Results

Table 3.2 displays the emission factors for fine particle mass, organic and elemental carbon, ionic species and key elemental species from the fireplace combustion of the Midwestern woods studied. The fine particle mass emission factors averaged 6.0 g kg⁻¹ of wood burned and ranged from 2.8 to 9.3 g kg⁻¹ over the six wood species tested. This result is comparable to the 5.3 g kg⁻¹ and 4.3 g kg⁻¹ average fine particle mass

Table 3.2. Fine Particle Mass Emission Factors and Chemical Composition for the Fireplace Combustion of Selected Midwestern U.S. Wood Species

	<u>Hardwoods</u>				<u>Softwoods</u>	
	White Oak	Sugar Maple	Black Oak	American Beech	Black Cherry	White Spruce
Fine Particle Mass (g kg ⁻¹ wood burned)	6.8 ± 1.4	4.0 ± 0.4	7.2 ± 1.3	9.3 ± 1.0	2.8 ± 0.4	5.6 ± 0.9
Elemental and Organic Carbon (Wt % of Fine Particle Mass)						
Organic Carbon (OC)*	75.6 ± 4.0	103.4 ± 5.6	76.0 ± 4.0	73.9 ± 3.9	67.8 ± 4.0	89.6 ± 4.7
Elemental Carbon (EC)	1.1 ± 0.2	4.6 ± 0.6	2.3 ± 0.3	1.1 ± 0.2	1.5 ± 0.4	3.5 ± 0.4
Ionic Species (Wt % of Fine Particle Mass)						
Chloride	0.24 ± 0.03	0.27 ± 0.02	0.26 ± 0.03	0.09 ± 0.01	0.78 ± 0.13	0.19 ± 0.01
Nitrate	0.29 ± 0.04	0.38 ± 0.03	0.25 ± 0.04	0.23 ± 0.02	0.71 ± 0.18	0.21 ± 0.02
Sulfate	0.46 ± 0.05	0.33 ± 0.03	0.46 ± 0.05	0.18 ± 0.02	0.44 ± 0.19	0.11 ± 0.02
Ammonium	0.03 ± 0.01	0.09 ± 0.01	0.05 ± 0.02	0.03 ± 0.01	0.11 ± 0.05	0.05 ± 0.01
Elemental Species (Wt % of Fine Particle Mass)						
Silicon	0.009 ± 0.001	<0.013	0.014 ± 0.002	0.008 ± 0.001	0.055 ± 0.004	0.009 ± 0.002
Sulfur	0.138 ± 0.002	0.094 ± 0.003	0.104 ± 0.002	0.083 ± 0.002	0.170 ± 0.005	0.056 ± 0.002
Chlorine	0.193 ± 0.005	0.260 ± 0.006	0.218 ± 0.005	0.068 ± 0.003	0.835 ± 0.015	0.184 ± 0.004
Potassium	0.904 ± 0.005	0.657 ± 0.006	1.028 ± 0.005	0.400 ± 0.004	1.902 ± 0.014	0.421 ± 0.004
Zinc	0.005 ± 0.001	0.020 ± 0.001	0.008 ± 0.001	0.002 ± 0.0003	0.012 ± 0.001	0.072 ± 0.001
Calcium	<0.013	<0.013	<0.023	<0.007	<0.003	0.015 ± 0.002
Bromine	0.001 ± 0.0003	0.002 ± 0.0003	0.001 ± 0.0002	0.001 ± 0.0002	0.006 ± 0.001	0.002 ± 0.0002
Rubidium	0.001 ± 0.0003	<0.001	0.001 ± 0.0002	0.003 ± 0.0002	0.012 ± 0.001	<0.012
Lead	<0.002	0.009 ± 0.001	<0.003	<0.004	0.019 ± 0.002	<0.002

*results will include adsorption of gas phase organics onto the quartz-fiber filter which may explain weight percents greater than 100

The following elements were not quantified because they fell below their respective blank levels: Al, Fe, Cu, Mn, Ni, Ag, P, Cr

The following elements were not found at quantities exceeding detection limits: Ti, V, Co, Ga, As, Se, Sr, Y, Zr, Mo, Pd, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl,

U

emission factor determined previously from the combustion of Northeastern and Southern U. S. wood species (20, 21). While these values are considerably lower than the USEPA emission factor for fireplace wood combustion of 17.3 grams PM per kilogram wood burned (32), our results are comparable to several previous results of the fine particle emissions from fireplaces which show emission factors ranging from 3 to 15 g kg⁻¹ of wood burned (33-36).

Over 67% of the fine particle mass in the emissions from every wood species studied consists of organic carbon (see Table 3.2). Conversion from organic carbon mass to total organic compound mass is accomplished using a scale factor that typically ranges between 1.2 and 1.4 in order to account for the oxygen, hydrogen, nitrogen and sulfur content of the compounds (37). Applying such a scale factor to the OC data in Table 3.2 results in a mass overbalance for several of the wood species which is most likely caused by organic vapor adsorption onto the quartz fiber filters (38). Other major species in the wood smoke include elemental carbon (1-5%) and potassium (0.4-1.9%). While potassium is often used as a tracer for wood smoke, there are other major sources including food cooking, cigarette smoke, airborne plant fragments, and the natural organic matter in paved road dust. As will be seen shortly, more specific wood smoke markers can be found among the individual organic compounds quantified here.

The detailed organic compound speciation profiles for the six Midwestern wood smokes sampled are given in Table 3.3 in terms of milligrams of each compound per gram of fine particle organic carbon emitted. Mass balances on the major organic compound classes emitted in the smokes from each wood species tested are shown in Figures 3.1-3.3. In these figures, all identified organic compounds were summed within

Table 3.3. Detailed Speciation of Fine Particle Organic Compounds Emitted from Midwestern U.S. Wood Species (all values expressed as mg g⁻¹ organic carbon (OC) emitted)

Compound	Hardwoods				Softwoods		Notes
	White Oak	Sugar Maple	Black Oak	American Beech	Black Cherry	White Spruce	
n-Alkanes							
n-nonadecane	0.017	0.068	-	0.029	+	0.016	b
n-eicosane	0.071	0.124	0.036	0.099	0.146	0.037	a
n-heneicosane	0.110	0.151	0.059	0.193	0.213	0.093	b
n-docosane	0.170	0.075	0.075	0.302	0.133	0.095	a
n-tricosane	0.149	0.089	0.083	0.164	0.079	0.073	b
n-tetracosane	0.107	0.053	0.037	0.150	0.029	0.035	a
n-pentacosane	-	0.034	0.030	0.033	0.025	0.015	b
n-hexacosane	-	0.045	-	0.011	-	-	b
n-heptacosane	-	0.054	-	-	-	-	b
n-Alkenes							
1-nonadecene	-	0.050	-	0.041	0.044	-	b
1-eicosene	0.097	0.257	0.025	0.502	0.260	0.100	b
1-heneicosene	0.139	0.156	0.073	0.304	0.383	0.084	b
1-docosene	0.517	0.112	0.164	1.491	0.252	0.440	b
1-tricosene	0.194	0.074	0.116	0.254	0.166	0.042	b
1-tetracosene	0.437	0.138	0.097	0.942	-	0.226	b
1-pentacosene	0.917	0.023	0.098	3.025	0.085	0.377	b
1-hexacosene	0.114	0.152	0.021	0.101	-	0.040	b
1-heptacosene	0.696	0.129	0.074	1.289	-	0.364	b
1-triacontene	-	0.138	-	-	-	-	b
n-Alkanols							
n-heptadecanol	-	-	-	0.028	0.391	-	a
n-octadecanol	-	0.030	0.039	-	0.123	0.042	a
n-nonadecanol	0.128	0.027	0.048	0.111	0.644	-	a
n-eicosanol	1.266	0.014	0.166	0.051	0.191	0.154	a
n-Alkanals							
n-eicosanal	-	-	-	0.046	-	-	b
n-heneicosanal	0.121	0.069	0.102	0.215	-	0.042	b
n-docosanal	0.313	0.093	0.249	0.536	0.051	0.148	b
n-tricosanal	0.339	0.086	0.296	0.187	0.040	0.097	b
n-tetracosanal	0.168	0.080	0.161	0.137	-	0.130	b
n-pentacosanal	0.069	-	0.078	-	-	-	b
Alkanoic Acids							
n-undecanoic acid	+	0.023	-	0.045	0.075	+	b,d
n-dodecanoic acid	0.105	0.167	0.106	0.130	0.368	+	a,d
n-tridecanoic acid	0.048	0.029	0.032	0.064	0.090	0.032	b,d
n-tetradecanoic acid	0.224	0.251	0.271	0.185	0.528	+	a,d
n-pentadecanoic acid	0.190	0.164	0.136	0.330	0.576	0.180	b,d
n-hexadecanoic acid	1.803	1.777	1.907	1.068	3.448	1.102	a,d
14-methylhexadecanoic acid	0.005	+	+	+	+	0.235	b,d
n-heptadecanoic acid	0.156	0.083	0.080	0.160	0.244	0.102	b,d
n-octadecanoic acid	0.428	0.297	0.352	0.252	1.387	0.341	a,d
16-methyloctadecanoic acid	-	-	0.004	-	-	0.069	b,d
n-nonadecanoic acid	0.074	0.033	0.031	0.127	0.086	0.088	b,d
n-eicosanoic acid	0.289	0.177	0.155	0.439	0.287	1.256	a,d
n-heneicosanoic acid	0.301	0.083	0.109	0.376	0.304	0.148	b,d
n-docosanoic acid	1.055	0.999	0.494	3.514	0.636	4.725	a,d
20-methyldocosanoic acid	-	-	-	-	-	0.039	b,d
n-tricosanoic acid	0.602	0.273	0.198	0.467	0.116	0.235	b,d
n-tetracosanoic acid	4.752	1.102	1.746	4.337	0.264	3.983	b,d
n-pentacosanoic acid	0.456	0.162	0.131	0.111	0.078	0.043	b,d

Compound	Hardwoods				Softwoods		Notes
	White Oak	Sugar Maple	Black Oak	American Beech	Black Cherry	White Spruce	
n-hexacosanoic acid	3.576	0.233	1.978	0.273	-	0.104	b,d
n-heptacosanoic acid	0.328	0.022	0.083	0.046	-	-	b,d
n-octacosanoic acid	0.142	0.018	0.166	-	-	-	b,d
Alkenoic Acids							
hexadecenoic acid	0.177	0.085	0.051	0.232	0.387	0.188	b,d
cis-9-octadecenoic acid	1.279	0.529	1.049	0.855	2.303	0.932	a,d
trans-9-octadecenoic acid	0.195	0.215	0.156	0.231	0.295	0.210	b,d
2-octadecenoic acid	0.081	-	0.044	0.111	0.145	0.054	b,d
9,12-octadecadienoic acid	1.605	1.436	4.037	1.280	2.571	1.286	a,d
nonadecenoic acid	0.074	-	-	-	-	-	b,d
eicosenoic acid	0.315	0.085	0.087	0.457	0.282	0.133	b,d
heneicosenoic acid	0.062	-	-	-	0.024	-	b,d
docosenoic acid	0.237	0.121	0.092	0.989	0.620	0.089	b,d
tricosenoic acid	0.055	-	-	-	-	-	b,d
tetracosenoic acid	1.715	0.019	0.601	0.503	-	-	b,d
pentacosenoic acid	0.160	-	-	0.148	-	-	b,d
hexacosenoic acid	1.198	-	0.136	-	-	-	b,d
Alkanedioic Acids							
hexanedioic acid	0.104	0.175	0.139	0.159	0.385	0.114	a,d
heptanedioic acid	0.041	0.056	0.052	0.086	0.230	0.036	a,d
octanedioic acid	0.092	0.064	0.061	0.150	0.480	0.105	a,d
nonanedioic acid	0.277	0.092	0.198	0.287	0.396	0.202	b,d
decanedioic acid	0.065	0.026	0.065	0.068	0.133	0.039	a,d
hexadecanedioic acid	0.281	0.084	0.082	1.450	1.952	0.649	b,d
octadecanedioic acid	0.140	-	0.038	0.326	0.168	0.118	b,d
eicosanedioic acid	0.113	-	0.030	0.265	0.070	0.506	b,d
docosanedioic acid	0.074	-	-	0.301	0.305	0.296	b,d
tetracosanedioic acid	0.233	-	0.170	0.075	-	-	b,d
pentacosanedioic acid	0.119	-	-	-	-	-	b,d
hexacosanedioic acid	0.279	-	0.198	-	-	-	b,d
heptacosanedioic acid	0.091	-	0.096	-	-	-	
Methyl Alkanoates							
methyl hexadecanoate	0.105	0.127	0.065	0.084	0.221	0.022	a
methyl 14-methylhexadecanoate	0.038	-	-	-	-	0.017	b
methyl heptadecanoate	0.018	0.008	0.012	0.021	0.037	-	b
methyl octadecanoate	0.030	0.027	0.042	0.026	0.050	0.016	a
methyl nonadecanoate	0.010	-	-	-	-	-	b
methyl eicosanoate	0.022	0.017	0.023	0.036	0.018	0.021	b
methyl heneicosanoate	0.013	0.007	0.011	0.034	0.033	-	b
methyl docosanoate	0.064	0.185	0.060	0.249	0.046	0.081	b
methyl tricosanoate	0.057	0.015	0.025	0.031	0.014	-	b
methyl tetracosanoate	0.331	0.164	0.140	0.184	0.041	0.087	b
methyl pentacosanoate	0.042	0.007	0.024	0.023	-	-	b
methyl hexacosanoate	0.200	0.028	0.141	0.014	-	-	b
methyl heptacosanoate	0.021	-	0.016	-	-	-	b
methyl octacosanoate	-	-	0.011	-	-	-	b
Ethyl Alkanoates							
ethyl docosanoate	-	-	-	-	-	0.081	b
ethyl tetracosanoate	0.015	-	-	-	-	0.161	b
ethyl hexacosanoate	0.010	-	-	-	-	0.006	b
Methyl Alkenoates							
methyl cis-9-octadecenoate	0.064	0.047	0.084	0.066	0.091	0.035	a
methyl 9,12-octadecadienoate	0.075	0.118	0.204	0.057	0.118	0.122	b
methyl eicosenoate	-	-	0.034	-	-	-	b
methyl docosenoate	0.040	0.023	0.023	0.081	0.116	0.016	b
methyl tetracosenoate	0.124	0.048	0.118	0.143	0.066	-	b

Compound	Hardwoods					Softwoods	Notes
	White Oak	Sugar Maple	Black Oak	American Beech	Black Cherry	White Spruce	
methyl hexacosenoate	0.126	-	0.031	-	-	-	b
Guaiacol and Substituted Guaiacols							
guaiacol	0.177	0.139	0.238	0.203	0.439	0.267	a
eugenol	0.079	0.138	0.072	0.056	0.131	0.123	a
cis-isoeugenol	0.051	0.125	0.057	0.017	0.034	0.094	a
trans-isoeugenol	0.328	1.133	0.448	0.167	0.340	0.681	b
4-vinylguaiacol	0.239	0.233	0.305	0.220	0.572	0.334	b
4-ethylguaiacol	0.064	0.070	0.070	0.027	0.078	0.104	a
4-propylguaiacol	0.024	0.034	0.022	0.013	0.025	0.050	a
vanillic acid	4.476	1.571	3.799	2.757	5.978	7.413	a
methyl vanillate	0.057	0.238	0.043	0.226	+	0.137	a
homovanillic acid	13.441	3.631	13.749	8.098	10.566	28.392	a
methyl homovanillate	0.079	0.174	0.075	0.182	0.165	0.127	a
vanillin	1.614	4.631	2.116	3.543	3.977	3.516	a
acetovanillone	1.634	5.628	1.813	4.184	3.197	3.305	a
propiovanillone	0.872	1.661	0.920	1.447	1.572	1.759	b
guaiacyl acetone	4.859	12.258	5.987	8.824	9.091	9.508	b
coniferyl aldehyde	18.651	23.693	29.449	26.180	19.913	37.624	a
Syringol and Substituted Syringols							
syringol	1.220	5.067	3.157	1.169	1.258	+	a
4-ethylsyringol	1.479	11.350	2.215	7.455	5.627	+	b
4-propylsyringol	0.980	6.521	1.366	4.735	5.121	0.030	b
methoxyeugenol	2.690	14.137	2.540	9.963	9.579	0.102	b
cis-methoxy-isoeugenol	1.884	7.544	3.462	7.285	2.605	0.248	b
trans-methoxy-isoeugenol	7.339	16.145	18.386	27.748	7.207	0.240	b
syringic acid	5.383	1.711	7.861	3.453	8.111	-	a
syringaldehyde	18.592	26.572	31.708	32.547	33.125	3.956	a
acetosyringone	4.323	6.511	11.324	11.451	11.628	1.737	a
syringyl acetone	12.066	19.325	34.400	32.246	31.785	3.592	b
propionyl syringol	1.643	1.986	3.261	2.665	2.215	0.322	b
sinapyl aldehyde	7.668	18.301	15.334	16.684	9.649	0.277	a
Other Substituted Benzenes and Phenols							
1,2-benzenediol (pyrocatechol)	2.885	2.087	5.674	11.049	3.994	5.432	b
1,4-benzenediol (hydroquinone)	0.360	1.656	12.610	9.739	5.705	4.719	a
1,3-benzenediol (resorcinol)	6.234	1.014	5.340	3.242	2.850	1.541	a
methyl benzenediols	2.317	2.364	5.651	8.439	2.967	6.607	b
methoxybenzenediols	2.793	2.269	6.788	5.607	2.402	0.460	c
hydroxybenzaldehydes	0.699	1.628	1.145	2.061	1.877	0.886	a
cinnamaldehyde	0.371	0.836	0.869	0.149	0.361	0.742	b
benzenetriols	2.701	-	27.913	0.257	0.863	2.015	b
hydroxyacetophenones	0.659	0.811	0.855	0.962	1.338	0.859	b
methyl hydroxybenzoates	0.114	0.209	0.118	0.340	0.156	0.070	b
trimethoxybenzenes	2.430	11.512	3.114	4.540	4.182	+	b
3,4,5-trimethoxybenzoic acid	-	0.341	6.691	7.337	64.841	0.960	a
phenyl acetic acid	0.062	0.069	0.083	0.072	0.135	+	b,d
phenyl propanoic acid	0.021	0.031	0.019	0.048	+	+	b,d
Dimers and Lignans							
diguaiacyl ethanes (divanillyls)	5.984	3.261	5.613	4.461	4.219	14.978	b
syringyl guaiacyl ethane	3.296	1.795	3.764	2.368	2.120	0.023	b
disyringyl methane	0.677	0.264	1.088	0.587	0.319	0.001	b
disyringyl ethane	6.790	3.566	11.725	4.523	5.275	-	b
shonanin (2-deoxo-matairesinol)	1.282	0.063	0.794	0.488	0.264	4.718	c
methyl-2-deoxomatairesinol	-	-	-	-	-	0.074	c
matairesinol	0.035	-	-	-	-	0.059	c
conidendrin	-	-	-	-	-	0.015	c

Compound	Hardwoods					Softwoods	Notes
	White Oak	Sugar Maple	Black Oak	American Beech	Black Cherry	White Spruce	
PAH and Alkyl PAH							
phenanthrene	0.041	0.059	0.043	0.060	+	0.057	a
anthracene	0.008	0.017	0.009	0.012	0.010	0.014	a
3-methylphenanthrene	0.011	0.015	0.009	0.037	+	0.015	b
2-methylphenanthrene	0.012	0.021	0.013	0.055	+	0.031	b
2-methylanthracene	0.008	0.014	0.010	0.039	0.007	0.013	a
9-methylphenanthrene	0.007	0.020	0.007	0.060	+	0.018	b
1-methylphenanthrene	+	+	+	0.038	+	0.040	a
phenylnaphthalenes	+	0.052	0.028	0.160	+	0.110	b
dimethyl or ethyl 178 MW PAHs	0.053	0.042	0.023	0.104	+	0.158	a
fluoranthene	0.217	0.351	0.241	0.638	+	0.233	a
acephenanthrylene	0.116	0.158	0.144	0.310	0.081	0.145	b
pyrene	0.244	0.366	0.283	0.673	+	0.258	a
methyl 202 MW PAHs	0.185	0.166	0.206	0.387	0.251	0.255	b
retene	+	+	+	+	+	1.340	a
benzo[ghi]fluoranthene	0.085	0.074	0.097	0.147	0.149	0.096	b
cyclopenta[cd]pyrene	0.121	0.095	0.162	0.304	0.148	0.141	b
benz[a]anthracene	0.110	0.089	0.127	0.227	0.232	0.138	a
chrysene	0.128	0.096	0.139	0.232	0.224	0.153	a
methyl 226 MW PAHs	0.028	0.019	0.035	0.064	0.051	0.040	b
methyl 228 MW PAHs	0.027	0.015	0.026	0.052	0.045	0.041	b
benzo[b]fluoranthene	0.056	0.041	0.076	0.108	0.106	0.075	a
benzo[k]fluoranthene	0.065	0.048	0.077	0.133	0.137	0.079	a
benzo[j]fluoranthene	0.032	0.021	0.039	0.062	0.048	0.040	b
benzo[e]pyrene	0.039	0.030	0.048	0.079	0.075	0.044	b
benzo[a]pyrene	0.076	0.059	0.095	0.160	0.151	0.095	a
perylene	0.011	0.006	0.011	0.021	0.019	0.012	a
indeno[1,2,3-cd]fluoranthene	0.016	0.011	0.021	0.027	0.030	0.018	b
indeno[1,2,3-cd]pyrene	0.059	0.041	0.069	0.106	0.121	0.067	a
benzo[ghi]perylene	0.038	0.026	0.045	0.072	0.071	0.041	a
anthanthrene	0.016	0.010	0.019	0.027	0.021	0.017	b
dibenz[a,h]anthracene	0.005	0.002	0.007	0.011	0.008	0.007	a
coronene	0.149	0.061	0.179	0.234	0.199	0.150	a
Oxy-PAH							
1,4-naphthalenedione	0.008	0.017	0.009	0.021	0.005	0.008	b
1-naphthol	0.090	0.106	0.091	0.532	0.091	0.074	a
2-naphthol	0.185	0.273	0.189	0.929	0.264	0.184	a
methylnaphthols	0.708	0.785	0.738	2.149	1.135	0.889	b
methoxynaphthols	0.078	0.216	0.069	0.321	+	0.139	a
fluorenone	0.123	0.127	0.120	0.206	+	0.068	a
1-H-phenalen-1-one	0.313	0.287	0.579	0.423	0.157	0.452	a
9,10-anthracenedione	0.082	0.099	0.097	0.112	0.060	0.071	a
xanthone	0.041	0.053	0.036	0.053	0.042	0.040	a
benzanthrone	0.110	0.084	0.191	0.206	0.133	0.181	a
Sugar Derivatives							
1,4:3,6-dianhydro- α -D-glucopyranose	+	7.271	2.539	3.039	+	2.334	c
galactosan	4.842	2.040	6.452	2.208	12.299	10.427	a
mannosan	7.610	8.519	9.994	4.536	17.371	35.845	a
levoglucosan	97.971	168.398	233.789	76.172	334.417	141.877	a
monomethylinositol	-	-	-	-	-	0.995	c
Coumarins and Flavonoids							
coumarin	0.047	0.088	0.051	0.078	0.103	0.060	a
umbelliferone	0.361	-	-	-	-	-	a
methoxyhydroxycoumarin	1.024	-	-	-	0.982	-	b
tetramethoxyisoflavone	0.644	0.639	1.684	1.053	0.704	0.043	b

Compound	Hardwoods				Softwoods		Notes
	White Oak	Sugar Maple	Black Oak	American Beech	Black Cherry	White Spruce	
Furans							
5-hydroxymethyl-2-furaldehyde	5.372	18.484	20.913	7.972	25.842	24.138	a
5-acetoxymethyl-2-furaldehyde	0.067	0.726	0.246	0.038	0.130	0.220	a
dibenzofuranols	0.288	0.180	0.443	0.358	0.482	0.337	a
benzonaphthofurans	0.192	0.200	0.200	0.317	+	0.241	c
Resin Acids							
deisopropyldehydroabietic acid	+	-	-	-	-	0.140	b,d
16,17-bisnordehydroabietic acid	-	-	-	-	-	0.038	b,d
16-nordehydroabietic acid	+	-	-	-	-	0.037	b,d
secodehydroabietic acids	-	-	-	-	-	0.375	b,d
pimaric acid	+	-	-	-	-	1.132	a,d
sandaracopimaric acid	+	-	-	-	-	1.591	b,d
dehydroabietic acid	+	+	+	+	+	7.972	a,d
8,15-pimaradien-18-oic acid	+	-	-	-	-	0.392	b,d
isopimaric acid	+	-	-	-	-	2.769	a,d
levopimaric acid	+	-	-	-	-	1.399	b,d
abietic acid	+	-	+	-	-	33.122	a,d
7-oxodehydroabietic acid	+	+	+	-	+	0.392	b,d
abieta-6,8,11,13-tetraen-18-oic acid	+	+	+	-	-	1.924	b,d
abieta-8,11,13,15-tetraen-18-oic acid	+	-	+	-	-	0.569	b,d
abieta-6,8,11,13,15-pentaen-18-oic acid	+	-	-	-	-	0.315	b,d
neoabietic acid	-	-	-	-	-	0.106	b,d
7-oxoabieta-8,11,13,15-tetraen-18-oic acid	-	-	-	-	-	0.059	b,d
Other Diterpenoids							
19-norabieta-8,11,13-triene	-	-	-	-	-	0.018	b
18-norabieta-8,11,13-triene	-	-	-	-	-	0.027	a
19-norabieta-4,8,11,13-tetraene	-	-	-	-	-	0.119	b
18-norabieta-4(19),8,11,13-tetraene	-	-	-	-	-	0.065	b
dehydroabietane	-	-	-	-	-	0.007	c
methyl deisopropyldehydroabietate	-	-	-	-	-	0.005	c
pimarinal	-	-	-	-	-	0.093	c
methyl 8,15-pimaradien-18-oate	-	-	-	-	-	0.026	c
methyl isopimarate	+	-	-	-	-	0.080	a
methyl 16,17-bisnordehydroabietate	+	-	-	-	-	0.010	c
dehydroabietal	+	-	-	-	-	0.036	c
methyl 6,8,11,13-abietatetraen-18-oate	+	-	-	-	-	0.147	c
methyl 8,11,13,15-abietatetraen-18-oate	+	-	-	-	-	0.091	c
methyl dehydroabietate	+	-	-	-	-	0.401	a
methyl-7-oxodehydroabietate	+	-	-	-	-	0.060	b
manoyl oxide	-	-	-	-	-	0.002	c
Phytosteroids							
stigmasterol	0.435	1.286	0.731	0.282	0.193	0.173	a
β-sitosterol	2.780	2.817	6.477	2.927	6.762	8.683	a
stigmast-4-en-3-one (sitostenone)	1.298	0.051	1.476	0.489	0.296	0.339	a
stigmasta-3,5-dien-7-one	0.912	0.158	0.787	0.515	0.295	3.032	b
stigmasta-4,6-dien-3-one	0.743	0.040	0.470	0.165	0.086	0.264	b
stigmastan-3-ol	0.440	0.174	0.311	0.423	0.259	0.145	a
stigmastan-3-one	0.673	0.050	0.247	0.639	0.082	0.076	c
Triterpenoids							
friedelin	4.440	-	-	-	-	-	a
β-amyrone	0.072	-	-	-	0.009	-	b
β-amyrin	0.143	-	-	-	0.023	-	a
α-amyrone	0.046	-	-	-	0.026	-	b
α-amyrin	0.071	-	-	-	0.080	-	a
Other Compounds							
1-indanone	0.025	0.058	0.052	0.025	0.058	0.043	a

Compound	Hardwoods					Softwoods	Notes
	White Oak	Sugar Maple	Black Oak	American Beech	Black Cherry	White Spruce	
methyl indanones	0.019	0.099	0.041	0.012	0.039	0.065	b
squalene	0.150	0.319	0.281	0.084	0.766	0.086	a
α -tocopherol (vitamin E)	2.697	0.031	0.610	0.054	0.047	0.023	a
β -tocopherol	0.221	-	-	-	-	-	b
unresolved complex mixture (UCM)	407	255	343	402	437	387	b

^aIdentification and quantification based on authentic quantitative standard

^bIdentification and quantification based on authentic quantitative standards of compounds with similar structures and retention times

^cIdentification based on relative retention times, mass spectra interpretation, and/or mass spectra libraries, quantification based on TIC response of authentic quantitative standards for other compounds that have similar retention times, functional groups and degree of fragmentation

^dDetected and quantified as methyl ester analog in derivatized fraction

- not detected

+ detected but not quantified due to comparable levels found in blank samples

Figure 3.1. Organic compound mass balance for the fine particle emissions from the fireplace combustion of Midwestern U.S. oak species

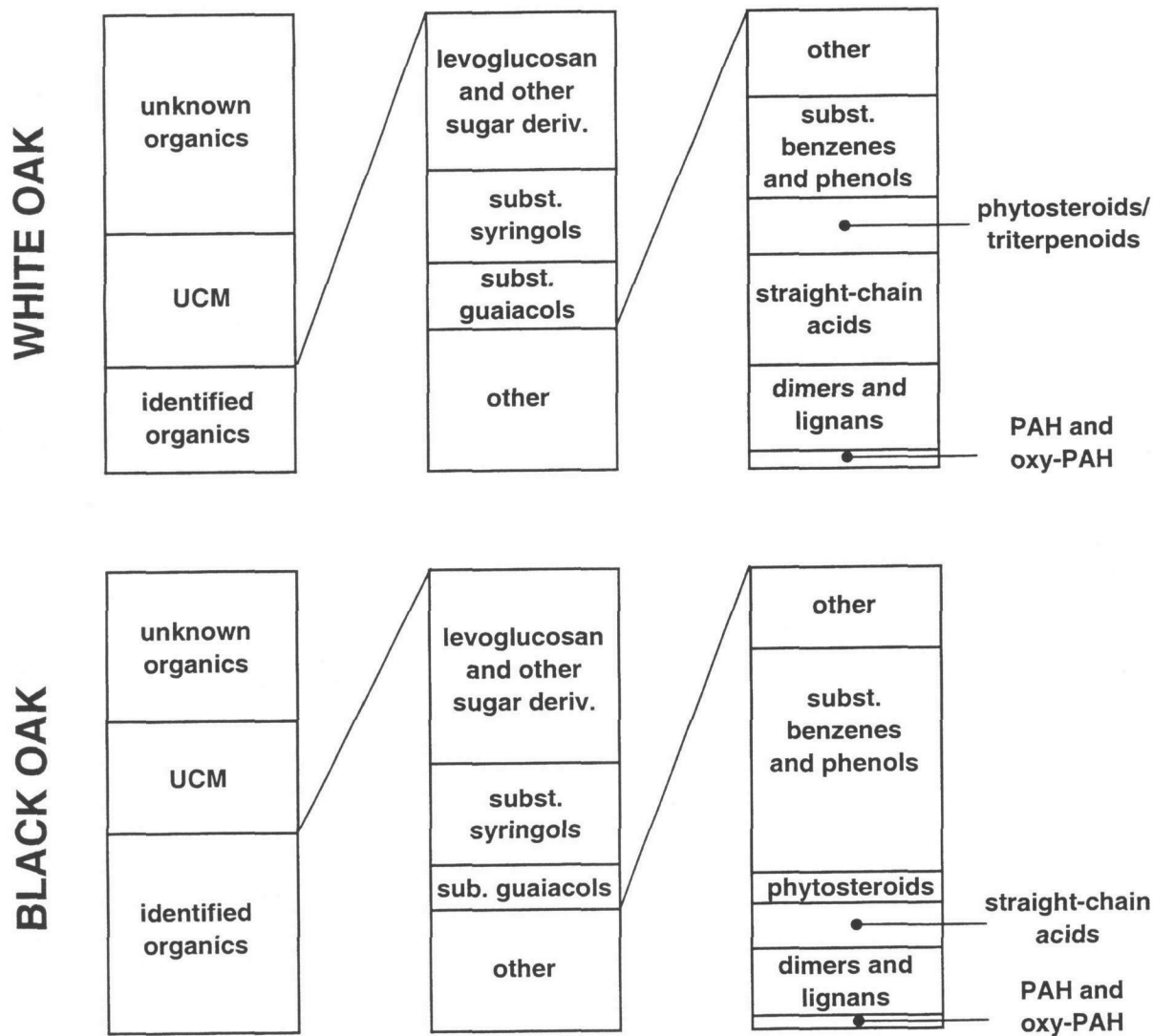


Figure 3.2. Organic compound mass balance for the fine particle emissions from the fireplace combustion of other Midwestern U.S. hardwood species

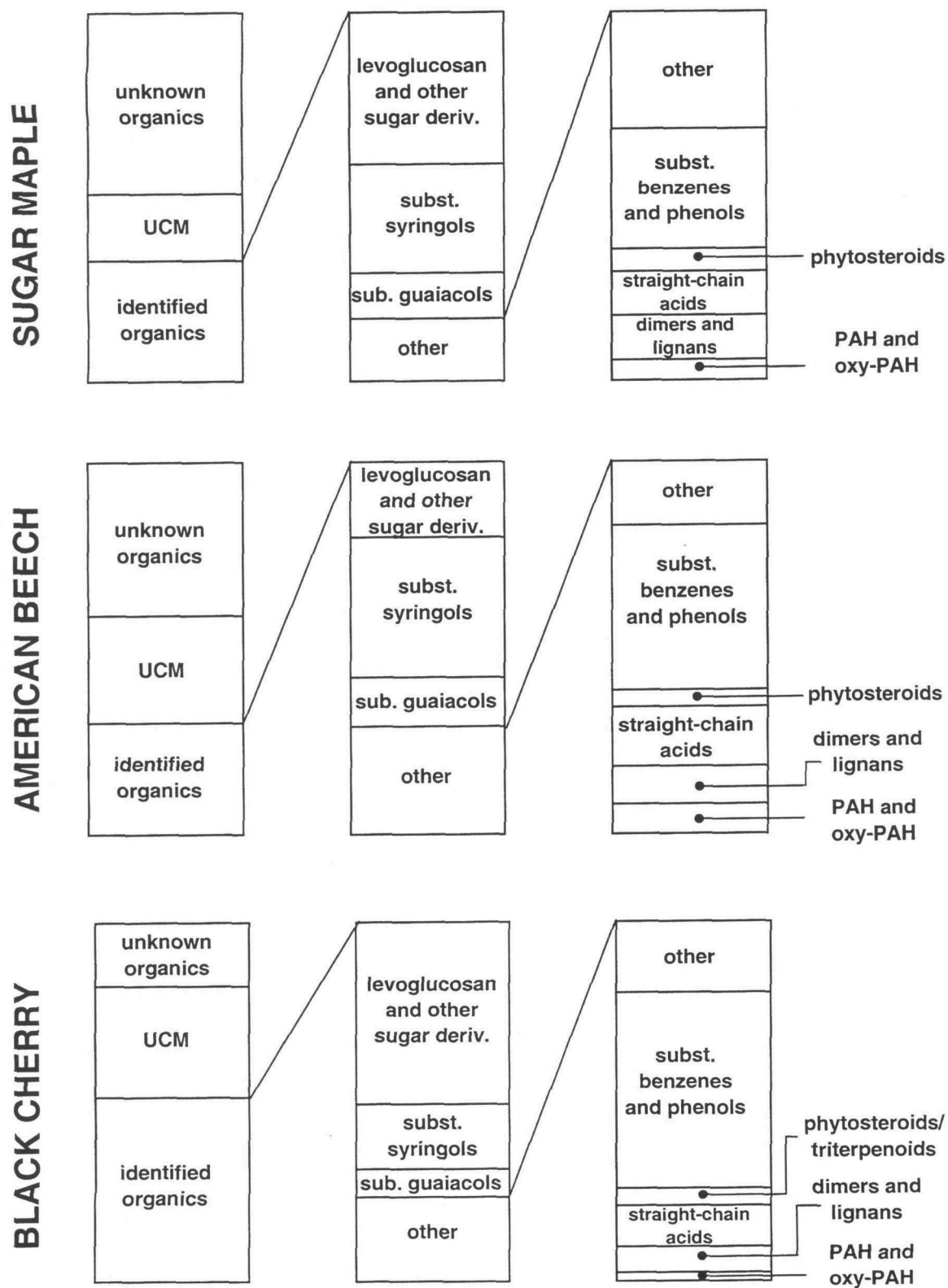
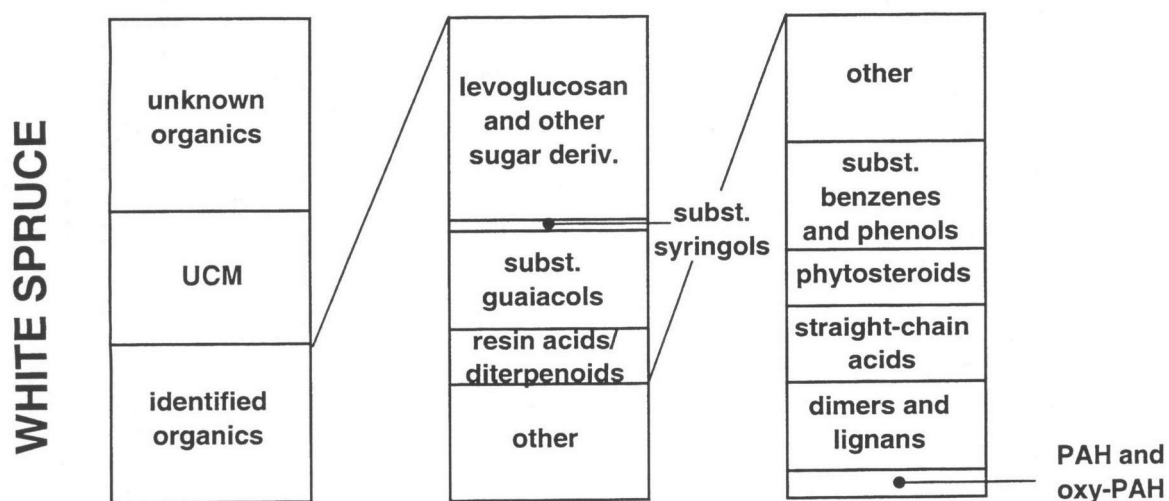


Figure 3.3. Organic compound mass balance for the fine particle emissions from the fireplace combustion of the Midwestern U.S. softwood species, white spruce



each compound class, and a conversion factor of 1.4 was used to convert organic carbon mass to estimated total organic compound mass.

Of the total organic compound mass emitted from burning each of the six woods, between 22-51% was identified and quantified as single organic compounds. The remaining mass consists largely of substituted syringols, substituted guaiacols, other phenolic compounds plus an unresolved complex mixture (UCM) of branched and cyclic organic compounds which passes through the GC column appearing as a hump underlying the resolved peaks. Levoglucosan, a sugar derivative formed as a pyrolysis product of cellulose (39), is by far the most abundant single compound measured, accounting for 5% to 24% of the fine particle organic compound emissions.

Levoglucosan is present at an average of 180 ± 100 mg per gram of fine particle organic carbon emitted, a somewhat higher value than seen in the previous two U. S. regional surveys that have been conducted to date (20, 21). Other important sugar derivatives quantified here include mannosan and galactosan. The high emission levels and uniqueness of these compounds to biomass combustion make them candidate molecular markers for biomass combustion (39).

Figures 3.1 and 3.2 show that for the two oak species as well as the other hardwoods, significant quantities of substituted syringols are found in the wood smokes. Figure 3.3 indicates that the softwood, white spruce, emits a much lower level of substituted syringols when burned and that significant quantities of resin acids and other diterpenoids are found in the softwood smoke that were not detected in the hardwood smokes. These differences between hardwood and softwood smokes correspond to the

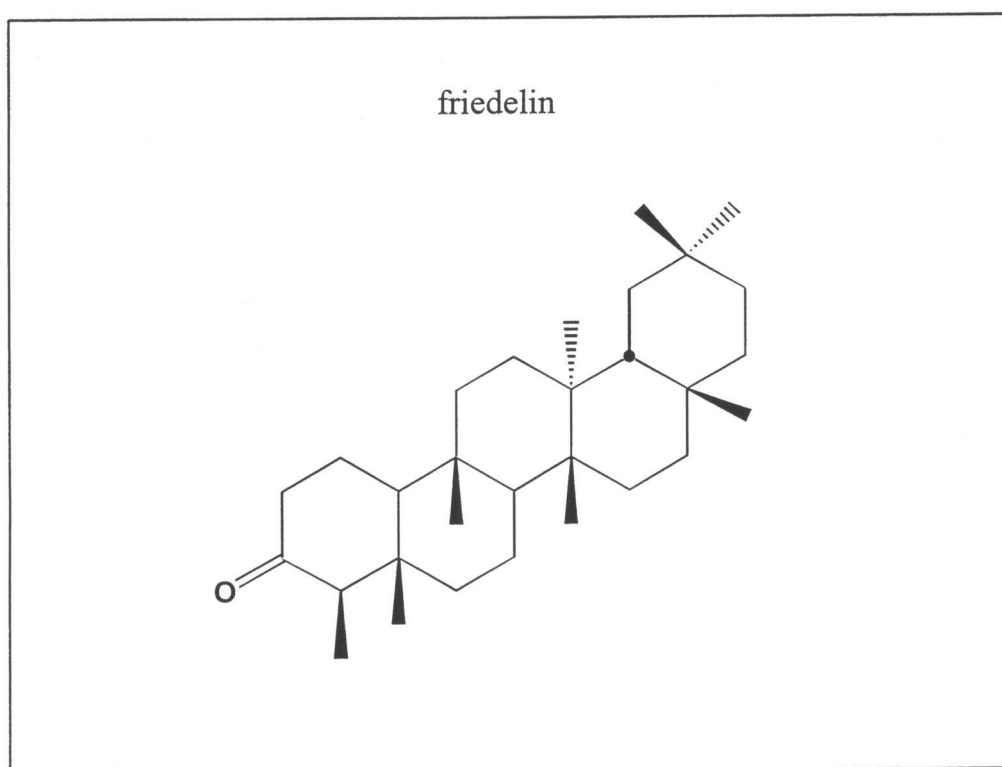
differences found previously (20, 21) and have been used in receptor models to differentiate between hardwood and softwood combustion (3).

A potential species-specific organic tracer for the combustion of white oak is the triterpenone, friedelin (Figure 3.4). In our study, the white oak smoke contained 4.4 mg of friedelin per gram of organic carbon. Of the 21 wood species examined in our entire source testing program, only white oak emitted friedelin in detectable quantities.

Friedelin is a known component of white oak bark (40) and has also been detected in the epicuticular leaf waxes from other oak species (41). While friedelin has been detected in black oak smoke previously (16), the present study is the first to quantify friedelin emissions in relation to the fine particle mass and other compounds emitted. We have not detected friedelin in any of the other oak species tested, including our tests of northern red oak and black oak. Given that friedelin is emitted in much greater quantities from white oak combustion than from the other oaks tested and given the great availability of white oak as firewood (See Table 3.1), it is logical to believe that white oak combustion dominates friedelin emissions to the atmosphere, at least among North American oak woods. Friedelin has been detected in atmospheric particle samples collected in the vicinity of residential wood burning or other biomass combustion sources indicating that it can be present in the environment at measurable concentrations (16). The dominance of white oak combustion as a source of friedelin and the proven presence of friedelin in ambient samples make it an excellent candidate as an organic tracer for white oak combustion.

In addition to friedelin which may be a nearly unique marker for white oak smoke, Table 3.3 shows differences in the relative amounts of certain compounds emitted

Figure 3.4. Chemical structure of friedelin ($C_{30}H_{50}O$), a potential species-specific organic tracer for white oak combustion



that may be used to distinguish between different wood types. Like the previous results for Northeastern and Southern U. S. wood species (20, 21), only small amounts of alkanes and alkenes are emitted from the combustion of Midwestern wood species. The peak in the homologous series of the n-alkanes occurs generally between carbon numbers 21 and 23. Unusually high levels of pentacosene and heptacosene were found in the American birch smoke and, to a lesser degree, in the white oak smoke. Small amounts of n-alcohols and n-alkanals were also found in the smoke from all of the woods tested, with relatively high levels of n-eicosanol present in the white oak smoke.

Alkanoic acids also were quantified in the smoke of the woods tested. The homologous series of the n-alkanoic acids generally is present over the range of carbon numbers from C_{11} to C_{28} and exhibits a preference for the even carbon number homologues as is also found in other wood smokes (20, 21). Hexadecanoic acid was present at high concentrations in all of the wood smokes as is typical of previous wood smoke analyses (19-21). The two oak species smokes contained relatively high levels of tetracosanoic and hexacosanoic acids while American beech and white spruce smokes were enriched in docosanoic and tetracosanoic acids. Prominent alkenoic acids found in all the wood smokes were cis-9-octadecenoic acid and 9,12-octadecadienoic acid, with white oak smoke containing comparatively high levels of tetracosenoic and hexacosenoic acids. The differences in the carbon number distributions of these straight chain acids, such as the enrichment of C_{24} and C_{26} acids in the two oak wood smokes, may prove useful in differentiating between different wood smokes. Alkanedioic acids as well as methylated or ethylated alkanoic and alkenoic acids also were present in the six wood smokes studied here.

As was the case with the Northeastern and Southern U.S. wood smokes (20, 21), substituted guaiacols emitted when the Midwestern hardwood and softwood species are burned include vanillic acid, homovanillic acid, vanillin, acetovanillone, guaiacyl acetone and coniferyl aldehyde. Coniferyl aldehyde was the most abundant compound in this class in all Midwestern wood smokes. Substituted syringols were found to a much greater extent in the hardwood smokes than in the softwood smoke, as expected from previous investigations (14, 19, 20). Syringaldehyde and syringyl acetone were the most abundant substituted syringols in the Midwestern hardwood smokes with trans-methoxy-iso-eugenol, sinapyl aldehyde and acetosyringone also being emitted at high levels. The smoke from white spruce contained much lower levels of the substituted syringols, as expected for softwood species. Black cherry smoke contained comparatively high levels of 3,4,5-trimethoxybenzoic acid, while black oak smoke was heavily enriched in the benzenetriols. Divanillyls were present in the smoke from all of the woods studied; dimers with at least one syringyl group occur primarily in the smoke from hardwood species, and again help to distinguish between hardwood and softwood smokes. White spruce smoke contained significantly higher levels of the lignin, shonanin (2-deoxomatairesinol), than the other woods tested here.

More than 40 different PAH, alkyl PAH and oxy-PAH are present in these wood smokes, as shown in Table 3.3. Similarly to the Northeastern and Southern wood smokes (20, 21), retene, the fully aromatized thermal alteration product of the resin acids present in conifer woods, was the dominant hydrocarbon found in the softwood smoke with very little detected in the hardwood combustion emissions. Pyrene, fluoranthene, and coronene were among the most abundant of the remaining PAHs found in the wood

smokes. Ten oxy-PAH also were quantified in the wood smoke samples, with the methyl naphthols as the most abundant oxy-PAH emitted from the combustion of all six Midwestern woods.

While levoglucosan is the most prevalent sugar derivative emitted from wood combustion, other sugar derivatives present in the wood smokes include 1,4:3,6-dianhydro- α -D-glucopyranose, monomethylinositol, galactosan, and mannosan. Several furans, flavonoids, and coumarins were quantified in the Midwestern wood smokes. The furan, 5-hydroxymethyl-2-furaldehyde, was the most abundant among these compound classes.

Combustion of the softwood, white spruce, was the only species whose smoke contained quantifiable levels of resin acids and other diterpenoids, consistent with previously reported distinctions between hardwoods and softwoods (14, 20). Abietic acid and dehydroabietic acid were the most abundant compounds emitted within this class. The most abundant phytosterol present in all of the Midwestern wood smokes is β -sitosterol; it has been detected in ambient fine particle samples (39) making it another good candidate for a wood smoke tracer. White oak combustion emitted significantly greater amounts of vitamin E than any of the other 22 American woods tested and thus, vitamin E (α -tocopherol) may prove another useful molecular marker of white oak combustion.

These results reaffirm the specific tracers for biomass burning including levoglucosan and β -sitosterol; the taxonomic distinction between hardwoods and softwoods (conifers) by the occurrence of resin diterpenoids in the latter and syringol derivatives in the former, and show the presence of unique tracer compounds such as

friedelin which may make it possible to distinguish smoke from the combustion of specific tree species such as white oak.

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Chapter 4

Chemical Characterization of Fine Particle Emissions from the Fireplace Combustion of Woods Grown in the Western United States

4.1 Introduction

Fine particle emissions from the fireplace combustion of wood can make a significant contribution to ambient fine particle levels in the Western United States. Emissions inventories compiled by the U.S. Environmental Protection Agency show that in 1995, almost 5% of fine particle emissions in the Western United States came from burning wood in residential fireplaces and wood stoves (1). In certain states such as Washington, Oregon, and California, residential wood combustion can contribute 8-14% of total fine particle emissions (1). Residential wood burning activity can vary greatly between households and from day to day and thus, emissions inventory data are difficult to apply to specific pollution events that occur on time scales of hours or days. Alternative source-apportionment techniques, however, do exist that utilize chemical mass balance receptor models (2-4) which compute the best fit linear combination of the chemical species profiles of the primary particle emissions sources in a particular geographic area that is needed to reproduce the chemical composition of ambient fine particle samples. While non-mineral potassium and isotopically "contemporary" carbon have been suggested as tracers for wood smoke in receptor models (5-7), these potential tracers are also emitted by other major sources such as meat cooking (8), refuse incineration (6, 9), and abrasion products from leaf surfaces (10) and thus cannot be used as a unique wood smoke tracer in mass balance calculations.

The wide variety of particle-phase organic compounds emitted from wood combustion provides a rich source of possible chemical tracers for wood smoke which have previously been used in receptor modeling calculations (2, 3). Detailed organic speciation profiles for the fine particle emissions from fireplace wood combustion have been determined for several wood types of regional importance (11-20). In order to apply these source apportionment methods at the national scale, detailed fireplace wood combustion source profiles must be determined for all of the important wood types burned in the United States.

This paper concerning wood species found in the Western United States is the last of a series (20-22) that present the results from an extensive set of source tests conducted to characterize the particulate organic compound emissions from the fireplace combustion of wood. The results provide valuable information on the variability in wood smoke tracer emissions for those organic compounds that are currently used in receptor models as well as the identification of additional tracer compounds that are specific to the smoke from individual wood species. The differences in emissions that occur when different woods are burned can possibly be used to resolve ambient fine particle contributions from combustion of specific wood species and thus, from the specific geographic regions where those species are burned.

4.2 Experimental Methods

4.2.1 Wood Selection

The method for selecting the wood species tested in this study are described in a previous paper (20). By combining state-level residential wood burning activity (23) and

state-level forestry inventories on existing wood stands (24), and by assuming people burn wood that is available in their local region (25), a national ranking of the most commonly available wood species for residential combustion was achieved. The top 21 wood species ordered by an index equal to 100 times the nationwide firewood availability for a particular species divided by the total of all firewood availability in the United States. Our calculations do not take into account such factors as the general preference for hardwood over softwood, which woods are commercially sold as fuel, regulating agency guidelines on tree clearance, or intrastate population/tree distributions. Our resulting national list and rankings were used as a guide for wood species selection that ensured the inclusion of the most available wood species within our test program. Twenty-two wood species were chosen for testing including 18 of the top 21 most commonly available wood species in the United States; four additional species were chosen in order to address particular issues. Specimens of these woods were then collected from both commercial suppliers and forestry research groups across the U.S. In every case, experts at these facilities provided us with positive species identification.

The twenty-two woods chosen for testing were divided into four groups based on the geographical location in which they grow, although several of the species are found across more than one region. Four wood species found primarily in the Western United States, including one hardwood and three softwoods, are examined in detail in the present paper and are listed in Table 4.1 along with their corresponding scientific names, geographic ranges, and the average moisture content of each wood sample tested determined by a standard oven-drying method described previously (20).

Table 4.1. Western United States Wood Species Selected for Use in This Study

Tree Species	Scientific Name	Moisture Content of Tested Wood (dry basis)	U.S. Range	National Availability Ranking
Douglas Fir	<i>Pseudotsuga menziesii</i>	19%	Western U.S. mountain ranges including Cascades, Sierras, and Rockies	3
Ponderosa Pine	<i>Pinus ponderosa</i>	15%	Western U.S. mountain ranges from Washington to Montana south to New Mexico and S. California	7
Quaking Aspen	<i>Populus tremuloides</i>	54%	Rocky Mountain states plus areas of Washington, California, and New Mexico	14
Pinyon Pine	<i>Pinus edulis</i>	9%	Utah, Colorado, Arizona, and New Mexico	139

4.2.2 Source Tests

The source testing procedures employed here are described in detail in a previous paper (20). Wood samples were burned in a conventional residential masonry fireplace and smoke samples were taken from the chimney at a point approximately four meters above the fire. Burn times ranged between 95 and 153 minutes with between 5 and 10 kilograms of wood burned per test. The smoke was sampled with the dilution source sampler of Hildemann et al. (8, 20, 26) that provides sufficient dilution, cooling and residence time to approximate downwind atmospheric conditions in order to obtain an accurate representation of the partitioning of organic compounds between the gas and particle phases. Six cyclone separators (27) were deployed to collect only the particles with aerodynamic diameters smaller than 2.5 μm . The exact configuration of filter media on which fine particle were collected was also described in a previous paper (20). A combination of Teflon and quartz fiber filters collected samples which were subsequently analyzed for organic carbon (OC) and elemental carbon (EC) (28), gravimetric mass, ionic species by ion chromatography (IC) (29), elemental composition by X-ray fluorescence (XRF) analysis (30), and individual organic compounds by gas chromatography/mass spectrometry (GC/MS).

4.2.3 Organic Chemical Analyses

Organic compound speciation was accomplished using methods established previously by Mazurek et al. (31) and Rogge et al. (32) which are described in a previous work (20). Briefly, the quartz fiber filters are spiked with a mix of deuterated internal recovery standards and then extracted in a series of hexane (Fischer Optima Grade) and

benzene/isopropanol (2:1) (benzene: E&M Scientific; isopropanol: Burdick & Jackson) sonications. Extracts are filtered, combined, and reduced in volume to approximately 1 ml, and are split into two separate fractions. One fraction is then derivatized with diazomethane to convert organic acids to their methyl ester analogs which are more amenable to GC/MS identification and quantification. Both the derivatized and underivatized sample fractions are analyzed by GC/MS on a Hewlett-Packard GC/MSD (GC model 6890, MSD model 5973) using a 30 m x 0.25 mm diameter HP-5MS capillary column (Hewlett-Packard). 1-Phenyldodecane is used as a co-injection standard for all sample extracts and standard runs. Hundreds of authentic standards have been prepared for the positive identification and quantification of many of the organic compounds found in the current source test program. When quantitative standards cannot be obtained for a given compound or compound class, significant effort is made to obtain a non-quantitative secondary standard that can be used for unique identification of the organic compounds. When a secondary standard is not available, interpretation of mass spectra and mass spectral libraries is used to aid in identification. Quantification of compounds identified using secondary standards has been estimated from the response factors for compounds having similar retention times and chemical structure. Estimates of the quantity of a few remaining compounds are based on use of the response factor of compounds with similar polarities, degrees of fragmentation, and retention times.

4.3 Results

Table 4.2 lists the emission factors for fine particle mass, organic and elemental carbon, ionic species and key elemental species from the fireplace combustion of the four

Table 4.2. Fine Particle Mass Emission Factors and Chemical Composition for the Fireplace Combustion of Selected Western U.S. Wood Species

	<u>Hardwoods</u>		<u>Softwoods</u>	
	Quaking Aspen	Douglas Fir	Ponderosa Pine	Pinyon Pine
Fine Particle Mass (g kg ⁻¹ wood burned)	8.0 ± 1.1	4.0 ± 0.8	6.0 ± 1.0	8.1 ± 1.0
Elemental and Organic Carbon (Wt % of Fine Particle Mass)				
Organic Carbon (OC)*	66.7 ± 3.5	96.5 ± 5.2	90.1 ± 4.8	79.7 ± 4.2
Elemental Carbon (EC)	1.1 ± 0.2	5.2 ± 0.6	7.3 ± 0.7	32.5 ± 1.9
Ionic Species (Wt % of Fine Particle Mass)				
Chloride	0.10 ± 0.01	0.24 ± 0.02	0.20 ± 0.02	0.04 ± 0.01
Nitrate	0.17 ± 0.01	0.30 ± 0.03	0.31 ± 0.02	0.07 ± 0.02
Sulfate	0.20 ± 0.01	0.58 ± 0.03	0.20 ± 0.02	0.09 ± 0.02
Ammonium	0.03 ± 0.01	0.16 ± 0.01	0.07 ± 0.01	0.05 ± 0.01
Elemental Species (Wt % of Fine Particle Mass)				
Silicon	0.008 ± 0.001	0.025 ± 0.002	0.019 ± 0.002	0.161 ± 0.003
Sulfur	0.057 ± 0.001	0.085 ± 0.002	0.102 ± 0.002	0.085 ± 0.002
Chlorine	0.069 ± 0.003	0.241 ± 0.006	0.198 ± 0.005	0.052 ± 0.003
Potassium	0.446 ± 0.003	0.366 ± 0.005	0.438 ± 0.005	0.159 ± 0.003
Zinc	0.071 ± 0.001	0.009 ± 0.001	0.075 ± 0.001	0.011 ± 0.001
Calcium	0.030 ± 0.002	0.031 ± 0.003	0.014 ± 0.003	<0.008
Bromine	<0.001	0.001 ± 0.0003	0.001 ± 0.0003	0.002 ± 0.0003
Rubidium	0.0008 ± 0.0001	<0.002	<0.001	<0.001
Lead	0.003 ± 0.001	<0.003	<0.004	<0.003

*results will include adsorption of gas phase organics onto the quartz-fiber filter which may explain weight percents greater than 100
The following elements were not quantified due to high blank levels: Al, Fe, Cu, Mn, Ni, Ag, P, Cr
The following elements were not found at quantities exceeding detection limits: Ti, V, Co, Ga, As, Se, Sr, Y, Zr, Mo, Pd, Cd, In, Sn, Sb, Ba, LA, Au, Hg, Tl, U

Western woods. The fine particle mass emissions ranged from 4.0 to 8.1 grams per kilogram of wood burned and averaged 6.5 g kg^{-1} over all six wood species tested. This result is comparable to the average fine particle mass emission factors determined previously from the combustion of Northeastern, Southern, and Midwestern U. S. wood species of 5.3 g kg^{-1} , 4.3 g kg^{-1} and 6.0 g kg^{-1} respectively (20-22). While less than the USEPA emission factor for fireplace wood combustion of 17.3 grams $\text{PM}_{2.5}$ per kilogram wood burned (33), our results are also comparable to several previous results for the fine particle emissions from fireplaces (19, 34-36).

The results in Table 4.2 also indicate that organic carbon contributes over 66% of the fine particle mass in the emissions from every wood species studied. A true mass balance requires conversion from organic carbon mass to total organic compound mass using a factor that accounts for the hydrogen, oxygen, and sometimes nitrogen and sulfur content of the organic compounds present. This scale factor typically ranges between 1.2 and 1.4 for typical atmospheric samples (37) or higher depending primarily on the oxygen content of the compounds. Applying such a scale factor to the OC data in Table 4.2 results in a mass overbalance for several of the wood species which is most likely caused by organic vapor adsorption onto the quartz fiber filters (38). The elemental carbon content of the fine particle emissions show very high variability as was observed in the woods from the other U. S. regions (20-22). The very high EC emissions from pinyon pine may be due to the dried sap that was observed on the logs prior to burning. The same relationship between visible sap content and EC emissions was observed for the combustion of eastern white pine from the Northeastern U. S. region (20). Potassium is often used as a marker for wood smoke (2, 5), and Table 4.2 shows varying results for

potassium emissions from the six wood types ranging from 0.16 to 0.45 weight % of the fine particle mass. However, considering the other non-wood combustion sources of fine particle potassium (8), potassium may be difficult to use as a wood smoke tracer.

Better candidates for wood combustion markers can be found in the over 250 organic compounds identified and quantified in the fine particle emissions from the Western U. S. wood species burned in this study. Emitted compounds are either volatilized components of the original natural molecules in the wood that recondense into the particle phase or pyrolysis products of the combustion reactions. The detailed organic compound speciation profiles for the four Western wood smokes characterized here, stated in terms of milligrams of each compound per gram of fine particle organic carbon emitted, are shown in Table 4.3. Figures 4.1 and 4.2 illustrate some of these differences through construction of a carbon compound mass balance based on major organic compound classes found in the smokes through GC/MS analysis. In these figures, all identified organic compounds were summed within each compound class, and a conversion factor of 1.4 was used to convert organic carbon mass to estimated total organic compound mass.

Between 15% and 39% of the total organic compound mass emitted from each of the six woods was identified and quantified. The remaining mass consists of an unresolved complex mixture (UCM) of branched and cyclic organic compounds which passes through the GC column appearing as a hump underlying the resolved peaks, plus an unknown organic fraction that includes compounds that either are not extractable in the organic solvents used here, are not elutable from the GC column, or that remain as unidentified peaks in the gas chromatograms. The pyrolysis product of cellulose,

Table 4.3. Detailed Speciation of Fine Particle Organic Compounds Emitted from Western U.S. Wood Species (all values expressed as mg g⁻¹ organic carbon (OC) emitted)

Compound	Hardwoods	Softwoods			Notes
	Quaking Aspen	Douglas Fir	Ponderosa Pine	Pinyon Pine	
n-Alkanes					
n-heptadecane	-	-	-	0.008	b
n-octadecane	-	-	-	0.010	a
n-nonadecane	0.015	0.058	0.031	0.020	b
n-eicosane	0.043	0.100	0.042	0.039	a
n-heneicosane	0.143	0.142	0.050	0.032	b
n-docosane	0.113	0.098	0.074	0.471	a
n-tricosane	0.220	0.088	0.058	0.036	b
n-tetracosane	0.078	0.034	0.016	-	a
n-pentacosane	0.208	0.023	-	-	b
n-hexacosane	0.058	0.005	-	-	b
n-heptacosane	0.223	0.031	-	-	b
n-octacosane	0.023	-	-	-	a
n-Alkenes					
1-nonadecene	-	0.041	-	-	b
1-eicosene	0.192	0.202	0.095	0.026	b
1-heneicosene	0.201	0.139	0.054	-	b
1-docosene	0.259	0.355	0.115	0.144	b
1-tricosene	0.206	0.068	-	-	b
1-tetracosene	0.174	0.171	0.107	0.134	b
1-pentacosene	0.145	0.106	0.039	0.035	b
1-hexacosene	0.220	-	-	-	b
1-heptacosene	0.127	0.083	-	0.047	b
1-octacosene	0.182	-	-	-	b
1-triacontene	0.530	-	-	-	b
n-Alkanols					
n-octadecanol	-	-	0.207	-	a
n-nonadecanol	0.031	-	-	-	a
n-eicosanol	1.020	0.023	-	-	a
n-Alkanals					
n-eicosanal	0.104	-	-	-	b
n-heneicosanal	0.163	0.028	-	-	b
n-docosanal	0.221	0.106	-	-	b
n-tricosanal	0.263	0.042	-	-	b
n-tetracosanal	0.395	0.033	-	-	b
n-pentacosanal	0.065	-	-	-	b
n-hexacosanal	0.995	-	-	-	b
n-octacosanal	0.886	-	-	-	b
Alkanoic Acids					
n-octanoic acid	+	+	+	0.370	a,d
n-decanoic acid	+	+	+	0.181	a,d
n-undecanoic acid	0.016	0.039	0.030	0.013	b,d
n-dodecanoic acid	0.106	0.124	0.159	0.088	a,d
n-tridecanoic acid	0.072	0.050	0.046	0.023	b,d
n-tetradecanoic acid	0.279	0.215	0.246	0.184	a,d
n-pentadecanoic acid	0.424	0.213	0.255	0.134	b,d
n-hexadecanoic acid	3.743	1.202	3.558	1.636	a,d
14-methylhexadecanoic acid	+	0.258	0.696	0.215	b,d

Compound	Hardwoods	Softwoods			Notes
	Quaking Aspen	Douglas Fir	Ponderosa Pine	Pinyon Pine	
n-heptadecanoic acid	0.234	0.098	0.194	0.065	b,d
n-octadecanoic acid	0.790	0.295	0.841	0.445	a,d
16-methyloctadecanoic acid	0.006	0.036	0.023	0.025	b,d
n-nonadecanoic acid	0.088	0.057	0.084	0.044	b,d
n-eicosanoic acid	0.964	0.343	1.642	0.222	a,d
n-heneicosanoic acid	0.355	0.063	0.187	0.033	b,d
n-docosanoic acid	3.288	1.272	3.424	0.775	a,d
20-methyldocosanoic acid	-	-	-	0.008	b,d
n-tricosanoic acid	0.908	0.076	0.159	0.050	b,d
n-tetracosanoic acid	4.818	1.451	4.310	0.462	b,d
n-pentacosanoic acid	0.468	0.022	0.061	0.012	b,d
n-hexacosanoic acid	3.114	0.070	0.582	0.044	b,d
n-heptacosanoic acid	0.106	-	-	-	b,d
n-octacosanoic acid	1.383	-	-	-	b,d
Alkenoic Acids					
hexadecenoic acid	1.051	0.152	0.219	0.068	b,d
cis-9-octadecenoic acid	0.668	0.417	16.605	3.623	a,d
trans-9-octadecenoic acid	0.169	0.090	1.254	0.496	b,d
2-octadecenoic acid	0.086	0.059	0.071	-	b,d
9,12-octadecadienoic acid	11.631	0.575	7.324	1.914	a,d
nonadecenoic acid	0.022	-	0.032	-	b,d
eicosenoic acids - 2 isomers	0.354	0.101	0.342	0.094	b,d
docosenoic acid	0.388	0.068	0.097	-	b,d
tetracosenoic acid	0.208	-	0.038	-	b,d
hexacosenoic acid	0.092	-	-	-	b,d
Alkanedioic Acids					
hexanedioic acid	0.136	0.142	0.148	0.061	a,d
heptanedioic acid	0.056	0.048	0.078	0.026	a,d
octanedioic acid	0.084	0.129	0.316	0.049	a,d
nonanedioic acid	0.415	0.220	1.108	0.092	b,d
decanedioic acid	0.058	0.027	0.122	0.009	a,d
undecanedioic acid	-	-	0.081	-	b,d
hexadecanedioic acid	1.640	0.550	0.616	0.058	b,d
octadecanedioic acid	0.244	0.096	0.219	-	b,d
eicosanedioic acid	0.055	0.102	0.363	0.023	b,d
docosanedioic acid	0.086	0.028	0.180	0.020	b,d
tetracosanedioic acid	0.041	-	-	-	b,d
Methyl Alkanoates					
methyl hexadecanoate	0.126	0.044	0.064	0.050	a
methyl 14-methylhexadecanoate	-	-	0.015	0.012	b
methyl heptadecanoate	0.017	0.008	0.008	0.006	b
methyl octadecanoate	0.042	0.025	0.023	0.020	a
methyl eicosanoate	0.062	0.019	0.011	0.021	b
methyl heneicosanoate	0.019	-	-	-	b
methyl docosanoate	0.224	0.046	0.026	0.050	b
methyl tricosanoate	0.047	-	-	-	b
methyl tetracosanoate	0.340	0.032	0.025	0.031	b
methyl pentacosanoate	0.037	-	-	-	b
methyl hexacosanoate	0.247	-	-	-	b
methyl octacosanoate	0.078	-	-	-	b

Compound	Hardwoods	Softwoods			Notes
	Quaking Aspen	Douglas Fir	Ponderosa Pine	Pinyon Pine	
Methyl Alkenoates					
methyl cis-9-octadecenoate	0.034	-	0.140	0.096	a
methyl 9,12-octadecadienoate	0.169	0.065	0.072	0.091	b
methyl docosenoate	0.060	-	-	-	b
methyl tetracosenoate	0.070	-	-	-	b
Guaiacol and Substituted Guaiacols					
guaiacol	0.184	0.161	0.217	0.152	a
eugenol	0.052	0.143	0.097	0.108	a
cis-isoeugenol	0.020	0.144	0.046	0.055	a
trans-isoeugenol	0.144	1.332	0.323	0.364	b
4-vinylguaiacol	0.218	0.276	0.179	0.183	b
4-ethylguaiacol	0.023	0.074	0.086	0.061	a
4-propylguaiacol	0.006	0.048	0.037	0.040	a
vanillic acid	3.829	3.727	2.366	0.684	a
methyl vanillate	0.047	0.330	0.221	0.201	a
homovanillic acid	3.724	10.215	11.170	10.784	a
methyl homovanillate	0.071	0.157	0.141	0.108	a
vanillin	2.414	7.919	3.890	4.146	a
acetovanillone	2.214	9.144	5.858	4.257	a
propiovanillone	0.786	2.969	2.173	1.583	b
guaiacyl acetone	4.073	14.108	10.723	7.043	b
coniferyl aldehyde	28.497	28.187	16.594	16.296	a
Syringol and Substituted Syringols					
syringol	0.489	0.328	+	+	a
4-ethylsyringol	1.123	0.964	0.114	0.080	b
4-propylsyringol	0.702	0.601	0.083	0.038	b
methoxyeugenol	4.588	1.739	0.267	0.130	b
cis-methoxy-isoeugenol	4.119	0.428	0.130	0.164	b
trans-methoxy-isoeugenol	20.563	1.259	0.046	0.020	b
syringic acid	5.210	-	-	-	a
syringaldehyde	24.871	9.869	4.536	2.668	a
acetosyringone	9.355	2.638	0.898	1.132	a
syringyl acetone	23.573	5.758	1.806	2.087	b
propionyl syringol	1.982	0.739	-	0.207	b
sinapyl aldehyde	17.344	1.848	-	0.685	a
Other Substituted Benzenes and Phenols					
1,2-benzenediol (pyrocatechol)	7.130	2.568	2.517	1.462	b
1,4-benzenediol (hydroquinone)	7.853	1.696	1.385	0.632	a
1,3-benzenediol (resorcinol)	2.540	1.525	0.648	0.365	a
methyl benzenediols	4.899	3.958	3.053	0.912	b
methoxybenzenediols	3.026	0.354	0.129	0.071	c
hydroxybenzaldehydes	1.592	2.027	0.959	0.887	a
cinnamaldehyde	0.121	1.348	0.914	1.444	b
benzenetriols	1.021	-	-	-	b
hydroxyacetophenones	0.689	0.962	0.813	0.620	b
methyl hydroxybenzoates	1.282	0.173	0.110	0.078	b
trimethoxybenzenes	1.336	0.759	0.118	0.084	b
3,4,5-trimethoxybenzoic acid	3.401	0.232	0.118	0.326	a
benzoic acid	0.168	+	+	0.135	a,d
phenyl acetic acid	0.052	0.105	0.080	0.082	b,d
phenyl propanoic acid	0.018	0.035	0.053	0.893	b,d

Compound	Hardwoods	Softwoods			Notes
	Quaking Aspen	Douglas Fir	Ponderosa Pine	Pinyon Pine	
Dimers and Lignans					
diguaiacyl ethanes (divanillyls)	3.454	6.883	9.631	5.077	b
syringyl guaiacyl ethane	2.208	0.092	-	0.027	b
disyringyl methane	1.260	0.010	-	-	b
disyringyl ethane	4.986	0.044	-	-	b
shonanin (2-deoxomatairesinol)	0.553	0.561	4.490	0.410	c
methyl-2-deoxomatairesinol	-	-	0.049	-	c
matairesinol	-	-	0.205	-	c
PAH and Alkyl PAH					
phenanthrene	+	0.089	0.053	0.169	a
anthracene	0.004	0.024	0.014	0.035	a
3-methylphenanthrene	0.010	0.027	0.017	0.051	b
2-methylphenanthrene	0.018	0.036	0.036	0.296	b
2-methylanthracene	0.009	0.024	0.020	0.047	a
9-methylphenanthrene	0.012	0.033	0.026	0.062	b
1-methylphenanthrene	0.015	0.029	0.066	0.465	a
phenylnaphthalenes	0.046	0.114	0.237	0.472	b
dimethyl or ethyl 178 MW PAHs	0.033	0.055	0.355	4.254	a
fluoranthene	0.276	0.482	0.318	0.551	a
acephenanthrylene	0.138	0.232	0.176	0.306	b
pyrene	0.286	0.488	0.349	0.570	a
methyl 202 MW PAHs	0.165	0.235	0.190	0.343	b
retene	+	+	3.550	6.818	a
benzo[ghi]fluoranthene	0.083	0.110	0.088	0.138	b
cyclopenta[cd]pyrene	0.128	0.165	0.133	0.164	b
benz[a]anthracene	0.123	0.136	0.110	0.197	a
chrysene	0.151	0.148	0.110	0.209	a
methyl 226 MW PAHs	0.032	0.040	0.028	0.038	b
methyl 228 MW PAHs	0.040	0.025	0.028	0.077	b
benzo[b]fluoranthene	0.065	0.086	0.066	0.099	a
benzo[k]fluoranthene	0.077	0.080	0.066	0.118	a
benzo[j]fluoranthene	0.037	0.035	0.036	0.043	b
benzo[e]pyrene	0.048	0.045	0.037	0.054	b
benzo[a]pyrene	0.094	0.093	0.075	0.124	a
perylene	0.011	0.010	0.011	0.019	a
indeno[1,2,3-cd]fluoranthene	0.021	0.015	0.014	0.026	b
indeno[1,2,3-cd]pyrene	0.066	0.063	0.058	0.088	a
benzo[ghi]perylene	0.046	0.036	0.035	0.050	a
anthanthrene	0.016	0.011	0.012	0.015	b
dibenz[a,h]anthracene	0.007	0.003	0.006	0.006	a
coronene	0.160	0.087	0.146	0.177	a
Oxy-PAH					
1,4-naphthalenedione	0.009	0.017	0.014	0.037	b
1-naphthol	0.205	0.125	0.085	0.046	a
2-naphthol	0.355	0.308	0.217	0.194	a
methylnaphthols	0.749	0.931	0.727	0.757	b
methoxynaphthols	0.134	0.359	0.223	0.165	a
fluorenone	0.098	0.123	0.094	0.263	a
1-H-phenalen-1-one	0.303	0.363	0.257	0.588	a
9,10-anthracenedione	0.065	0.082	0.095	0.150	a
xanthone	0.052	0.049	0.036	0.045	a
benzanthrone	0.189	0.138	0.093	0.236	a

Compound	Hardwoods	Softwoods			Notes
	Quaking Aspen	Douglas Fir	Ponderosa Pine	Pinyon Pine	
Sugar Derivatives					
1,4:3,6-dianhydro- α -D-glucopyranose	2.068	8.027	4.997	2.926	c
galactosan	2.771	11.641	5.097	-	a
mannosan	12.908	60.862	20.633	1.513	a
levoglucosan	187.926	270.609	71.456	10.367	a
monomethylinositol	-	1.206	1.081	-	c
Coumarins and Flavonoids					
coumarin	0.062	0.080	0.040	0.076	a
methoxyhydroxycoumarin	0.339	-	-	-	
pinostrobin chalcone	-	-	-	0.702	b
tetramethoxyisoflavone	0.931	-	-	-	b
Furans					
5-hydroxymethyl-2-furaldehyde	22.707	40.537	19.308	6.639	a
5-acetoxymethyl-2-furaldehyde	0.055	1.300	0.206	0.135	a
dibenzofuranols	0.261	0.257	0.184	0.218	a
benzonaphthofurans	0.192	0.282	0.281	0.395	c
Resin Acids					
deisopropyldehydroabietic acid	-	0.031	0.255	0.164	b,d
16,17-bisnordehydroabietic acid	-	0.009	0.051	0.801	b,d
16-nordehydroabietic acid	-	+	0.070	0.267	b,d
secodehydroabietic acids	-	0.023	0.275	0.301	b,d
pimaric acid	-	-	5.908	0.210	a,d
sandaracopimaric acid	-	0.220	1.343	3.135	b,d
dehydroabietic acid	+	2.079	8.531	6.771	a,d
8,15-pimaradien-18-oic acid	-	0.077	0.609	50.392	b,d
isopimaric acid	-	1.785	8.913	4.312	a,d
levopimaric acid	-	0.192	3.205	0.167	b,d
abietic acid	-	0.823	30.491	5.343	a,d
7-oxodehydroabietic acid	-	0.065	0.456	0.546	b,d
abieta-6,8,11,13-tetraen-18-oic acid	-	0.573	2.998	2.537	b,d
abieta-8,11,13,15-tetraen-18-oic acid	-	0.096	0.853	0.838	b,d
abieta-6,8,11,13,15-pentaen-18-oic acid	-	0.059	0.569	0.597	b,d
neoabietic acid	-	-	0.386	0.060	b,d
7-oxoabieta-8,11,13,15-tetraen-18-oic acid	-	0.005	0.059	0.084	b,d
Other Diterpenoids					
18-norisopimara-4(19),7,15-triene	-	-	0.015	0.008	b
19-norabieta-8,11,13-triene	-	0.009	0.025	0.268	b
18-norabieta-8,11,13-triene	-	0.013	0.047	0.448	a
19-norabieta-4,8,11,13-tetraene	-	0.055	0.264	0.631	b
18-norabieta-4(19),8,11,13-tetraene	-	0.026	0.133	0.305	b
dehydroabietane	-	0.007	0.011	0.085	c
methyl deisopropyldehydroabietate	-	-	0.021	0.069	c
pimarinal	-	-	1.011	0.000	c
methyl 8,15-pimaradien-18-oate	-	-	0.039	4.731	c
methyl isopimarate	-	+	0.121	0.487	a
methyl 16,17-bisnordehydroabietate	-	-	0.013	0.426	c
dehydroabietal	-	0.007	0.020	0.077	c
methyl 6,8,11,13-abietatetraen-18-oate	-	+	0.217	0.562	c
methyl 8,11,13,15-abietatetraen-18-oate	-	0.003	0.140	0.179	c
methyl dehydroabietate	-	+	0.554	1.450	a
methyl abietate	-	-	0.349	0.388	a
methyl-7-oxodehydroabietate	-	0.007	0.062	0.267	b

Compound	Hardwoods	Softwoods			Notes
	Quaking Aspen	Douglas Fir	Ponderosa Pine	Pinyon Pine	
manoyl oxide	-	0.057	-	0.349	c
Phytosteroids					
stigmasterol	0.195	-	-	-	a
β -sitosterol	12.364	1.776	0.685	1.286	a
stigmast-4-en-3-one (sitostenone)	0.300	0.042	0.046	0.040	a
stigmasta-3,5-dien-7-one	0.733	0.307	1.820	0.280	b
stigmasta-4,6-dien-3-one	0.255	0.047	0.030	0.063	b
stigmastan-3-ol	0.248	0.037	0.061	-	a
stigmastan-3-one	0.039	0.039	0.029	0.012	c
Triterpenoids					
β -amyron	0.058	-	-	-	b
β -amyrin	0.155	-	-	-	a
α -amyron	0.088	-	-	-	b
α -amyrin	0.316	-	-	-	a
Other Compounds					
1-indanone	0.017	0.062	0.040	0.071	a
methyl indanones	0.005	0.188	0.081	0.100	b
squalene	0.391	0.149	0.088	0.099	a
α -tocopherol (vitamin E)	0.424	-	-	-	a
β -tocopherol	0.025	-	-	-	b
unresolved complex mixture (UCM)	324	264	356	387	b

^aIdentification and quantification based on authentic quantitative standard

^bIdentification and quantification based on authentic quantitative standards of compounds with similar structures and retention times

^cIdentification based on relative retention times, mass spectra interpretation, and/or mass spectra libraries, quantification based on TIC response of authentic quantitative standards for other compounds that have similar retention times, functional groups and degree of fragmentation

^dDetected and quantified as methyl ester analog in derivatized fraction

- not detected

+ detected but not quantified due to comparable levels found in blank samples

Figure 4.1. Organic compound mass balance for the fine particle emissions from the fireplace combustion of the Western U.S. hardwood species, quaking aspen

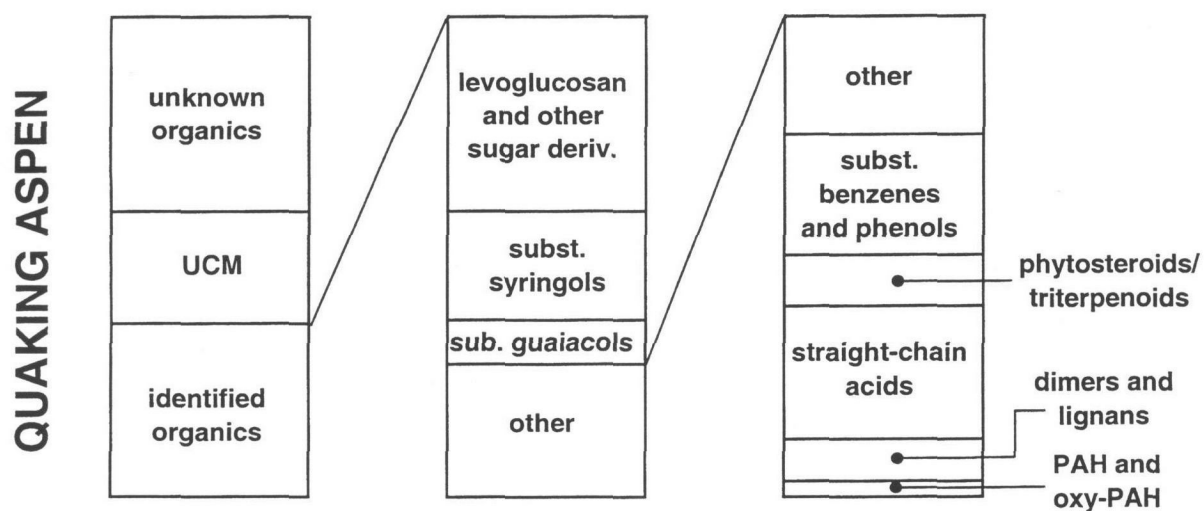
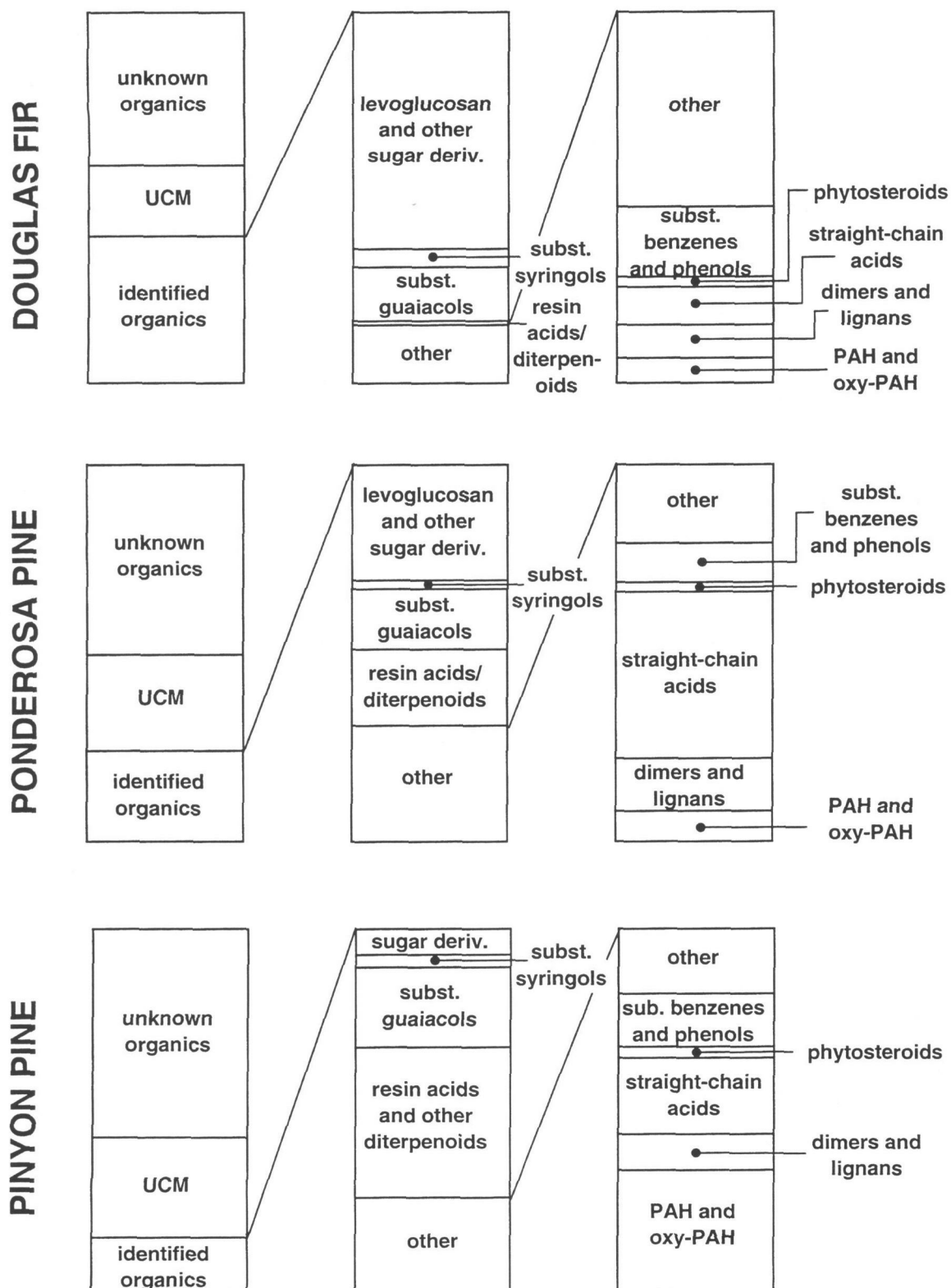


Figure 4.2. Organic compound mass balance for the fine particle emissions from the fireplace combustion of Western U.S. softwood species



levoglucosan, is by far the most abundant organic compound measured in all of the wood species with the exception of pinyon pine smoke, which had an unusual, and as yet unexplained, low levoglucosan content. Excluding pinyon pine, between 5% and 19% of the fine particle organic compound emissions are accounted for by levoglucosan, yielding an average of 180 ± 100 mg levoglucosan per gram of fine particle organic carbon emitted. The very high emission level and uniqueness of this compound to biomass combustion make it an important candidate as a marker for biomass combustion in general as has been proposed in previous studies (39).

Figure 4.1 shows that for the hardwood species, quaking aspen, significant quantities of substituted syringols are found in the wood smokes. Figure 4.2 indicates that the Western U. S. softwoods emit much lower levels of substituted syringols when burned. The emissions from ponderosa pine and pinyon pine combustion contained significant quantities of resin acids and other diterpenoids that were not detected in the hardwood smoke. These distinctions between hardwood and softwood smokes correspond to the differences found previously (20-22). However, the smoke from the other softwood, Douglas fir, contained much lower levels of resin acids and diterpenoids and somewhat higher levels of the substituted syringols than the two pine wood smokes. Thus, the distinctions between hardwoods and softwoods, which have been used in receptor models to differentiate between the two wood types (2, 3), may not be applicable to some softwoods such as Douglas fir.

A closer look at Table 4.3 reveals some additional differences in the relative amounts of certain compounds emitted that may be used to distinguish between different wood types. Like the previous results for the other three U. S. regions (20-22), only

small amounts of alkanes and alkenes are emitted from the combustion of Western wood species with the peak in the compound distributions occurring generally between carbon numbers 20 and 23. The exception is quaking aspen combustion, which emitted relatively higher amounts of n-pentacosane, n-heptacosane and 1-triacontene. Small quantities of n-alcohols and alkanals were also found in some of the woods tested with quaking aspen smoke containing more compounds from these classes than that of the three softwood species.

Alkanoic acids ranging from carbon numbers 8 to 28 were found in the smoke of the woods tested and exhibit the general even carbon number preference for acids found in natural materials (40) which was also found in the Northeastern, Southern, and Midwestern wood species smokes (20-22). Hexadecanoic, docosanoic and tetracosanoic acids were measured at relatively higher levels in all of the Western wood smokes. Quaking aspen combustion emitted hexacosanoic and octacosanoic acids to a greater extent than the other Western woods. The dominant alkenoic acids found in all the wood smokes were cis-9-octadecenoic acid and 9,12-octadecadienoic acid. The differences in the carbon number distributions of the alkenoic acids, such as the enrichment of 9,12-octadecadienoic acid in quaking aspen smoke and cis-9-octadecenoic acid in the smoke from burning ponderosa pine, may prove useful in differentiating the fine particle emissions from the combustion of different woods. Small amounts of alkanedioic acids as well as methylated alkanoic and alkenoic acids were also detected to varying degrees in the emissions from the combustion of the four wood types with similar carbon number preference patterns to those for the unesterified acids.

As was the case with the other U. S. Regional wood smokes (20-22), the predominant substituted guaiacols found in the smoke from the four Western wood species were vanillic acid, homovanillic acid, vanillin, acetovanillone, guaiacyl acetone and coniferyl aldehyde. Coniferyl aldehyde was the dominant compound in this class in all Western wood smokes. While both hardwoods and softwoods emitted substituted guaiacols at various levels, the substituted syringols were found to a much greater extent in the hardwood smoke as was described above. However, Douglas fir smoke contained more substituted syringols than the two pine wood smokes. Syringaldehyde and syringyl acetone were the most prevalent substituted syringols in all of the Western wood smokes with trans-methoxy-iso-eugenol, sinapyl aldehyde and acetosyringone also being emitted at high levels. Among other substituted benzenes, quaking aspen smoke contained higher levels of the benzenediols, methoxybenzenediols and 3,4,5-trimethoxybenzoic acid than that from the softwoods. Divanillyls were found in all the wood smoke samples but the dimers with at least one syringyl group were found primarily in the quaking aspen emissions showing the same distinction between hardwood and softwood smokes as was found for the single ring phenolics. Ponderosa pine smoke contained significantly higher levels of the lignin, shonanin (2-deoxo-matairesinol), than the other woods tested here.

PAHs are not major contributors to wood smoke mass emissions but many different PAH compounds can be quantified in wood smoke as shown in Table 4.3. Similarly to the wood smokes from the other U. S. regions (20-22), retene, the fully aromatized thermal alteration product of the resin acids present in conifer woods, was the dominant hydrocarbon found in the two pine smokes with very little detected in the hardwood combustion emissions. However, unquantifiable levels of retene were present

in the smoke from Douglas fir combustion further suggesting that Douglas fir smoke may not be as similar to the other softwoods as expected. Other than retene, pyrene and fluoranthene were among the most prevalent PAHs found in the wood smokes. Pinyon pine combustion emitted unusually high levels of the ethyl or dimethyl 178 molecular weight PAHs which could not be identified as individual compounds. Several oxy-PAH were also detected and quantified in the wood smoke samples with the methyl naphthols as the most abundant oxy-PAH emitted from the combustion of all four Western woods.

As discussed above, levoglucosan is the most prevalent sugar derivative emitted from wood combustion. Other sugar derivatives found at lower levels include 1,4:3,6-dianhydro- α -D-glucopyranose, monomethylinositol, galactosan, and mannosan. Pinyon pine combustion produced much less of the sugar derivatives than the other three woods. Several coumarins, flavonoids, and furans were also measured in the Midwestern wood smokes, with the dominant furan, 5-hydroxymethyl-2-furaldehyde, being emitted at significantly higher levels than the other compounds in these classes. Among all the woods from the U. S. that were examined in this study, the flavonoid, pinostrobin chalcone, was only detected in pinyon pine from the Western region and eastern white pine from the Northeastern region (20). The presence of this compound corresponds to the very high elemental carbon emissions seen in the smokes from these two woods and may be related to the visibly high sap content.

Resin acids and other diterpenoids were only emitted in appreciable quantities in the combustion of the softwood species and were not found at quantifiable levels in the smoke produced by the hardwood, quaking aspen. Once again, Douglas fir smoke differs from the other softwoods with significantly lower levels of the resin acids and

diterpenoids. Abietic acid was the predominant resin acid emitted by ponderosa pine combustion. The burning of pinyon pine produced extremely high levels of 8,15-pimaradien-18-oic acid comprising over 3% of the fine particle organic compound mass, over ten times higher than any of the other 21 American wood species tested (20-22). β -sitosterol was the most prevalent phytosterol measured in the quaking aspen smoke and was emitted at higher levels than was found in the smokes from the three softwood species. Since β -sitosterol has been detected in ambient fine particle samples (39), it is another good candidate for a wood smoke tracer.

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Chapter 5

Chemical Characterization of Fine Particle Emissions from the Wood Stove Combustion of Prevalent United States Wood Species

5.1 Introduction

U.S. Environmental Protection Agency emission inventories show that in the year 1995 approximately 12% of non-fugitive dust fine particle emissions in the United States were emitted from wood combustion in fireplaces and wood stoves (1). In certain local pollution events, more than half of the atmospheric fine particle concentration can be attributed to wood smoke (2). A brief calculation using U.S. Census figures on appliance ownership and heating practices (3) combined with state-level Department of Energy data on wood consumption (4) suggest that the amount of wood burned residually is divided almost equally between wood stoves and fireplaces. Other estimates indicate that as much as 72% of residential wood combustion occurs in wood stoves vs. fireplaces (5). Therefore, the particulate emissions from wood stoves, and any significant differences between the emissions from wood stoves and fireplaces, should be accounted for in regional control strategies aimed at residential wood combustion.

Source-apportionment techniques that utilize chemical mass balance receptor models can compute the contributions from the primary particle emissions sources to a particular ambient fine particle sample (2, 6, 7). These methods require a detailed chemical characterization of the fine particle mass emitted from each pollution source which then can be compared to the chemical composition of an ambient sample. Non-mineral potassium and “contemporary” carbon have been suggested as chemical tracers for wood smoke (8-10), but since these tracers are also emitted by other major sources

such as meat cooking (11) and refuse incineration (10, 12), they cannot be used as a unique wood smoke tracer in mass balance calculations. However, the particle-phase organic compounds emitted from wood combustion include numerous unique chemical tracers for wood smoke which have previously been used in receptor modeling calculations (2, 6).

Several previous studies of wood stove emissions have measured the emission factors for fine particle mass as well as for certain organic compound classes such as PAH, dioxins, and phenolic compounds (13-20).

The current study focuses on the wood stove combustion of the five most prevalent wood species in the United States. In addition to fine particle mass emissions, ionic and elemental composition, and carbon content, this work provides a detailed organic speciation profile which includes over 250 individual organic compounds. Since the same five wood species burned in the wood stove were also burned in previous studies of fireplace emissions (21-24), a direct comparison of the fine particle emission profiles from the two different combustion appliances is possible.

In 1988, the U. S. Environmental Protection Agency established New Source Performance Standards (NSPS) which required that all new wood stoves sold are certified to meet certain particulate emission limits by 1992 (25). Manufacturers responded by including a catalytic element in their wood stove designs or by designing high-efficiency wood stoves which reduce emissions with careful control of air flow and temperature. Current estimates indicate that about 40% of the new certifiable designs in use are catalytic stoves and 60% are non-catalytic high-efficiency stoves (26). However, due to the long lifetime of these appliances, only 11% of the wood stoves in use are EPA

certified (26). For this reason, the goal of this study is to investigate the emissions from the more common conventional technology non-certified wood stove. Since all new stoves must be certified, a catalyst equipped wood stove was acquired which allowed for operation in a non-catalytic mode, thus simulating a traditional wood stove with no emissions control technology. For two wood types, additional catalytic mode experiments were conducted to examine the effects of the catalyst on fine particle emissions.

5.2 Experimental Methods

5.2.1 Source Tests

A Vermont Castings, Inc., Encore Model #2190 catalyst-equipped wood stove was selected for the source tests and installed according to manufacturer specifications. The medium-sized stove with an approximately 2.7 ft³ (0.076 m³) firebox includes a primary air control lever to regulate stove temperature and a damper which directs flow through the catalyst. In accordance with the manufacturer's Owner's Guide, the air control was adjusted during the tests to maintain a stove-top temperature between 500-600°F (260-316°C) as measured by a surface thermometer. For the five non-catalytic mode tests, the flow was never directed through the catalytic element in order to simulate a traditional wood stove without emissions control technology. Two additional tests were conducted in catalytic-mode according to the Owner's Guide which directs the user to close the damper and engage the catalyst only after the stove-top temperature reaches 450°F (232°C).

The methodology for wood species selection is described in detail in a previous paper (23). Briefly, state-level residential wood combustion activity from the U. S. Department of Energy (4) was combined with state-by-state forestry surveys (27) to compile a list of the most available wood species in the U.S. The top five nationally available wood species were chosen for combustion in the wood stove and are listed in Table 5.1 along with their scientific names, geographical ranges, and moisture contents. Two wood species, Douglas fir and white oak, were also burned under catalytic conditions. The wood burned came from the same wood samples collected for previous fireplace emissions testing. However, due to a six month time lag, the moisture contents of the wood burned in the wood stove were less than those for the same wood species burned in the previous fireplace tests (21-24, 27). Methods for determining moisture content have also been described previously (23).

The wood was cut into logs of 6-12 inches (15-30 cm) in length with diameters between 3 and 5 inches (7-13 cm). Fires were ignited with 4-6 pieces of crumpled newspaper and small kindling pieces cut from the same wood species being burned. The stove doors were left open for a few minutes until the fire was well established. Burn times ranged between 112 and 148 minutes with between 3 and 4.5 kilograms of wood burned per test. Particle sampling began immediately prior to ignition and was ended when particle sizing instrumentation showed few additional particles being emitted, typically occurring 10 to 20 minutes after the formation of a smoldering fire with no visible flames. Smoke samples were taken through a port in the stove flue located approximately 3 meters above the wood stove.

Table 5.1. United States Wood Species Selected for Wood Stove Combustion Tests

Tree Species	Scientific Name	Moisture Content of Tested Wood (dry basis)	U.S. Range	National Availability Ranking
Red Maple	<i>Acer rubrum</i>	9%	Entire Eastern U.S.	1
Loblolly Pine	<i>Pinus taeda</i>	8%	From New Jersey to Texas including entire Southeastern U.S.	2
Douglas Fir*	<i>Pseudotsuga menziesii</i>	10%	Western U.S. mountain ranges including Cascades, Sierras, and Rockies	3
White Oak*	<i>Quercus alba</i>	14%	Entire Eastern U.S. west to S. Minnesota and south to E. Texas	4
Sugar Maple	<i>Acer saccharum</i>	13%	Northeastern and Midwestern U.S south to Missouri north to Minnesota	5

*species tested under both non-catalytic and catalytic conditions

The same advanced source sampling system used for the previous fireplace emissions studies was utilized for the wood stove tests. A detailed description of the configuration is provided in a previous paper (23). The dilution source sampler, developed by Hildemann et al. (28), dilutes hot stack emissions with a 25 to 45 fold excess of activated carbon-filtered and HEPA-filtered air. After sufficient residence time and cooling, organic vapors condense onto pre-existing particles yielding a more accurate representation of the partitioning of organic compounds between the gas and particle phases under atmospheric temperatures and concentrations. Smoke samples are withdrawn from the dilution source sampler through an array of AIHL-design cyclone separators (29) operated at the nominal flow required to achieve a 2.5 μm size cut. A pair of Teflon filters collect fine particle samples which are analyzed for gravimetric mass, ionic content by ion chromatography (IC) (30), and elemental composition by X-ray fluorescence (XRF) (31). Several quartz fiber filters (47 mm diameter, Pallflex tissue quartz 2500 QAO) collect samples which are analyzed for elemental and organic carbon (EC/OC) by thermal evolution/optical transmission methods (32) as well as individual organic compound speciation by gas chromatography/mass spectrometry (GC/MS).

5.2.2 Organic Chemical Analyses

Organic compound speciation of the wood stove samples was accomplished with the procedures developed by Mazurek et al. (33) and Rogge et al. (34). The methods are the same as those used for the previous fireplace emissions testing and are described in a paper concerning those tests (23). In short, quartz fiber filters containing fine particle samples are spiked with a suite of deuterated internal recovery standards. Solvent

extractions are performed by mild sonication twice in hexane (Fischer Optima Grade) and then three times in a benzene/isopropanol mixture (2:1) (benzene: E&M Scientific; isopropanol: Burdick & Jackson). Extracts are filtered, combined, and reduced in volume to a nominal volume of 1 ml. The concentrated extracts are then split into two separate volumes, one of which is then derivatized with diazomethane to convert organic acids to their methyl ester analogs. After further volume reduction, the derivatized and underivatized sample fractions are analyzed by GC/MS on a Hewlett-Packard GC/MSD (GC model 6890, MSD model 5972) using a 30 m x 0.25 mm diameter HP-5MS capillary column (Hewlett-Packard). A co-injection standard 1-phenyldodecane is used to normalize overall instrument response across all sample and standard runs. Hundreds of authentic standards have been prepared for the positive identification and quantification of many of the organic compounds found in the smoke from wood combustion. When quantitative standards cannot be obtained for a given compound, non-quantitative secondary standards are sometimes used for identification and the responses of other compounds with similar polarities, retention times, and degrees of fragmentation is used for quantification. Interpretation of mass spectra and mass spectral libraries are also used to aid in identification.

5.3 Results

Emission factors for fine particle mass from all seven wood stove source tests, including two catalytic tests, are listed in Table 5.2. Emission factors ranged between 0.88 and 3.4 grams fine particulate per kg of wood burned with a non-catalytic wood stove average of 1.8 g kg^{-1} wood burned. While the use of the catalytic element reduced

Table 5.2. Fine Particle Mass Emission Factors and Chemical Composition from Wood Stove Combustion

	Hardwoods						Softwoods	
	Red Maple	White Oak	White Oak	White Oak	Sugar Maple	Loblolly Pine	Douglas Fir	Douglas Fir
	no	no	yes	yes	no	no	no	yes
Catalytic Bed Engaged								
Fine Particle Mass (g kg ⁻¹ wood burned)	0.88 ± 0.16	3.4 ± 0.5	2.2 ± 0.4	1.4 ± 0.2	1.1 ± 0.2	1.2 ± 0.2		
Elemental and Organic Carbon (Wt % of Fine Particle Mass)								
Organic Carbon (OC)	59.4 ± 7.1	55.4 ± 3.2	55.1 ± 3.6	51.2 ± 3.1	43.6 ± 4.6	64.7 ± 6.0		
Elemental Carbon (EC)	22.8 ± 2.8	3.3 ± 0.3	10.4 ± 0.8	5.8 ± 0.5	13.4 ± 1.5	21.9 ± 2.1		
Ionic Species (Wt % of Fine Particle Mass)								
Chloride	1.32 ± 0.14	0.39 ± 0.02	0.48 ± 0.03	0.34 ± 0.02	0.35 ± 0.04	0.26 ± 0.04		
Nitrate	0.73 ± 0.10	0.38 ± 0.02	0.52 ± 0.03	0.43 ± 0.03	0.19 ± 0.05	0.24 ± 0.05		
Sulfate	0.55 ± 0.07	0.97 ± 0.03	1.37 ± 0.06	0.33 ± 0.03	0.18 ± 0.04	0.27 ± 0.04		
Ammonium	0.24 ± 0.03	0.05 ± 0.01	0.06 ± 0.01	0.14 ± 0.01	0.27 ± 0.03	0.16 ± 0.02		
Elemental Species (Wt % of Fine Particle Mass)								
Silicon	0.130 ± 0.014	0.0071 ± 0.0012	0.068 ± 0.004	0.034 ± 0.003	0.192 ± 0.018	0.146 ± 0.012		
Sulfur	0.169 ± 0.018	0.236 ± 0.006	0.508 ± 0.020	0.149 ± 0.005	0.099 ± 0.010	0.121 ± 0.010		
Phosphorus	<0.007	<0.003	<0.007	<0.005	<0.005	0.013 ± 0.002		
Chlorine	0.839 ± 0.089	0.278 ± 0.009	0.488 ± 0.022	0.366 ± 0.013	0.184 ± 0.017	0.199 ± 0.016		
Potassium	1.680 ± 0.180	1.514 ± 0.038	2.740 ± 0.100	1.014 ± 0.031	0.458 ± 0.041	0.621 ± 0.047		
Copper	<0.001	<0.001	0.0018 ± 0.0003	<0.001	<0.001	<0.001		
Zinc	0.047 ± 0.005	0.0055 ± 0.0005	0.014 ± 0.001	0.053 ± 0.002	0.048 ± 0.005	0.0094 ± 0.0016		
Manganese	<0.002	<0.001	<0.002	<0.002	<0.001	<0.002		
Bromine	0.0050 ± 0.0010	0.0014 ± 0.0003	0.0032 ± 0.0005	0.0042 ± 0.0004	0.0020 ± 0.0009	0.0021 ± 0.0009		
Rubidium	0.0074 ± 0.0009	0.0009 ± 0.0001	0.0014 ± 0.0003	<0.001	0.0011 ± 0.0003	<0.001		
Strontium	<0.001	<0.001	<0.001	<0.001	<0.001	0.0021 ± 0.0003		
Lead	<0.003	0.0013 ± 0.0004	0.0052 ± 0.0008	0.010 ± 0.001	<0.002	<0.003		

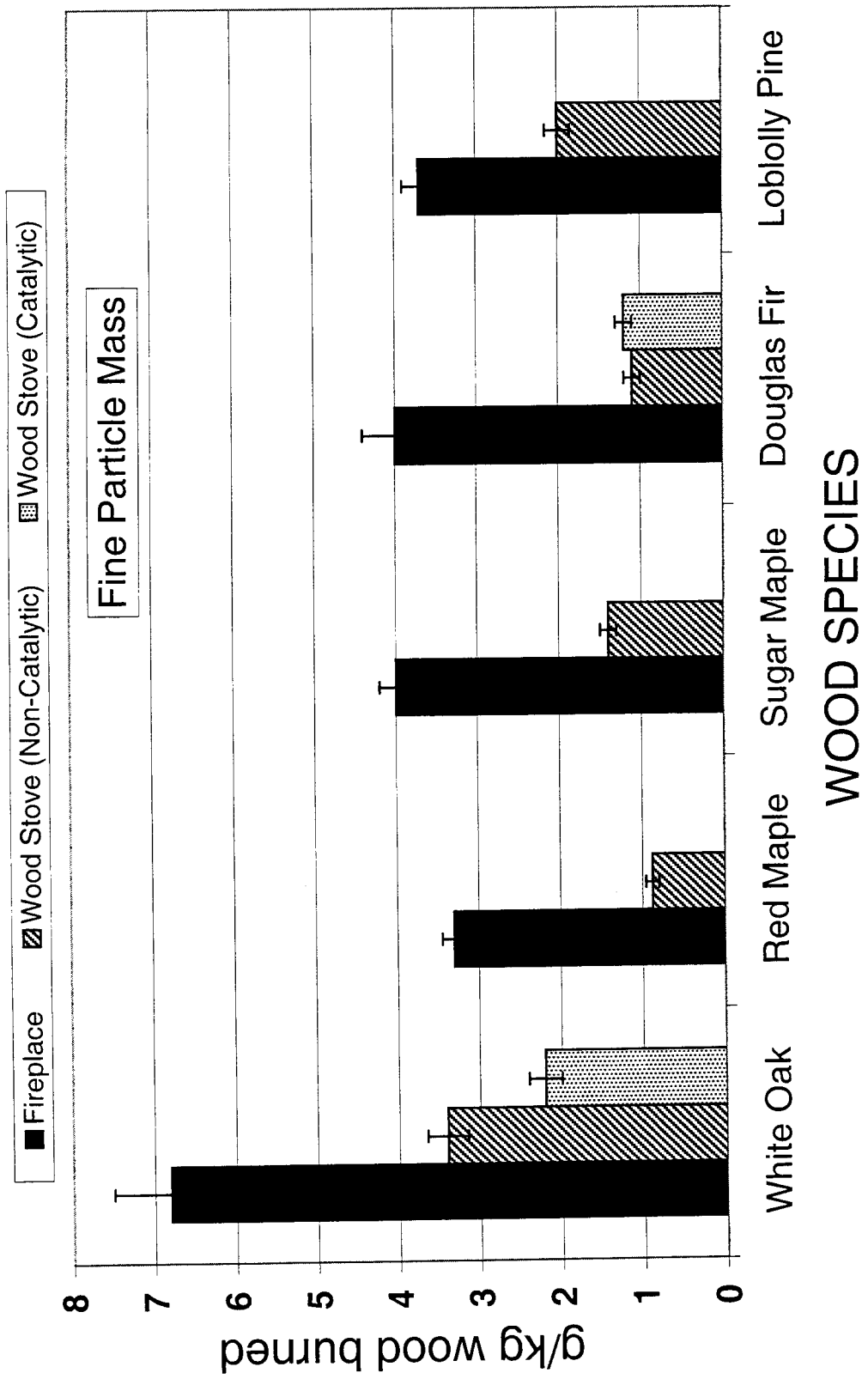
The following elements were not quantified due to high blank levels: Al, Fe

The following elements were not found at quantities exceeding detection limits: Ag, Ni, Cr, Ti, V, Co, Ga, As, Se, Y, Zr, Mo, Pd, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, U

the fine particle emission factor of white oak from 3.4 to 2.2 g kg⁻¹ wood burned, it did not significantly change the fine particle emission factor from Douglas fir. It has been reported that the large majority of fine particle mass emitted from wood stoves occurs in the start-up phase (35), a result supported by preliminary data from our particle sizing instrumentation. In the catalytic-mode tests, the catalyst was not engaged until after the stove had reached the prescribed operating temperature which occurred between 30 and 45 minutes after ignition. It is not surprising that the catalyst does not have a larger effect on fine particle mass emissions since most of the fine particle mass was most likely emitted prior to catalytic operation. Fine particle mass emissions factors from wood stoves depend on many factors including burn rate, firebox size, stove type, fuel type, and fuel moisture content (14, 19, 20). While some estimates of fine particle emission factors are comparable to our results, ranging from about 1 to 7 g kg⁻¹ wood burned (14, 18, 20), others are much higher surpassing 20 g kg⁻¹ wood burned (19). The wide uncertainty in fine particle emission factors from wood stoves suggests that chemical mass balance receptor techniques, which do not rely on overall emission factors, may be preferable in determining the impact of wood stoves on ambient fine particle levels. Figure 5.1 compares fine particle mass emission factors from the combustion of the same wood species in both fireplaces (21-24) and wood stoves. In general, wood stoves emit considerably less fine particulate matter than fireplaces.

Table 5.2 also shows that, as was the case with fireplace emissions (21-24), the fine particle mass emitted is composed primarily of organic compounds with the second largest component being elemental carbon. The elemental carbon content of the wood stove emissions are, with the exception of burning loblolly pine, generally higher than the

Figure 5.1. Comparison of fine particle mass emission factors from the combustion of U.S. wood species in a fireplace, a non-catalytic wood stove, and a catalytic wood stove



corresponding fireplace combustion test. Furthermore, the use of the catalyst tended to increase elemental carbon emissions, an expected result due to the secondary catalytic combustion which can further pyrolyze organic compounds into the more complete combustion product elemental carbon. The remaining emission factors in Table 5.2 are comparable to those determined from the fireplace tests of these wood species.

Potassium, often used as a wood smoke marker, was the most abundant element measured by XRF, but still exhibits a significant degree of variability among different wood species as was found in the fireplace tests (21-24).

The over 250 organic compounds listed in Table 5.3 provide a richer source of potential wood smoke markers. These compounds can be volatilized molecules of the original naturally occurring compounds in the wood that recondense into the particle phase or alternatively, chemical products of pyrolysis during combustion. Figures 5.2 and 5.3 depict an organic compound mass balance of the wood stove emissions based on the total organic compound mass divided into compound classes. The total organic compound mass was estimated by multiplying the organic carbon content by a factor of 1.4 to account for the additional mass of primarily hydrogen and oxygen present in the molecules (36). The total for each compound class is the sum of quantified organic compounds as determined by GC/MS. Compared to the previous results for fireplace emissions (21-24), more of the total organic compound mass was identifiable as either individual organic species or an unresolved complex mixture (UCM) in the wood stove combustion emissions. Wood stove combustion involves controlled air intake which acts to create an oxygen starved combustion process. It is possible that less highly polar organics with high oxygen content are produced by wood stoves vs. fireplaces. Since

Table 5.3. Detailed Speciation of Fine Particle Organic Compounds Emitted from Wood Stoves. Tests were conducted in non-catalytic mode unless otherwise specified (all values expressed as mg g⁻¹ organic carbon (OC) emitted).

Compound	Hardwoods				Softwoods			Notes
	White Oak	White Oak (Catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (Catalyst)	Loblolly Pine	
n-Alkanes								
n-heptadecane	-	-	-	-	0.021	0.013	-	b
n-octadecane	-	-	-	-	0.017	-	-	a
n-nonadecane	0.020	0.044	0.032	0.056	0.087	0.109	-	b
n-eicosane	0.073	0.092	0.076	0.122	0.064	0.042	0.038	a
n-heneicosane	0.108	0.126	0.114	0.275	0.210	0.207	0.071	b
n-docosane	0.173	0.164	0.110	0.160	0.141	0.225	0.107	a
n-tricosane	0.184	0.180	0.090	0.216	0.136	0.309	0.132	b
n-tetracosane	0.139	0.203	0.054	0.160	0.067	0.132	0.063	a
n-pentacosane	0.169	0.221	0.085	0.108	0.052	0.140	0.059	b
n-hexacosane	0.059	0.130	0.035	0.192	0.028	0.048	0.036	b
n-heptacosane	#	#	#	#	#	#	#	b
n-octacosane	0.023	0.052	0.034	0.025	#	#	0.019	a
n-nonacosane	0.024	0.067	0.028	-	0.008	0.009	0.021	b
n-Alkenes								
1-eicosene	0.165	0.373	0.259	0.263	0.245	0.115	-	b
1-heneicosene	0.116	0.145	0.144	0.283	0.201	0.234	0.047	b
1-docosene	0.590	0.455	0.240	0.297	0.410	0.977	0.323	b
1-tricosene	0.317	0.209	0.065	0.195	0.063	0.132	0.059	b
1-tetracosene	0.541	0.375	0.086	0.590	0.193	0.686	0.185	b
1-pentacosene	1.314	0.862	0.094	0.106	0.040	0.169	-	b
1-hexacosene	0.115	0.083	-	0.662	0.054	0.132	-	b
1-heptacosene	0.697	0.488	-	0.966	#	0.190	0.099	b
n-Alcohols								
n-octadecanol	-	0.173	-	-	-	-	-	a
n-nonadecanol	-	0.072	-	-	-	-	-	a
n-eicosanol	0.851	0.730	0.131	0.045	-	-	-	a
n-Alkanals								
n-heneicosanal	0.131	0.101	-	-	-	-	-	b
n-docosanal	0.286	0.247	0.068	0.098	-	0.042	-	b
n-tricosanal	0.276	0.159	0.102	#	-	0.047	-	b
n-tetracosanal	0.117	0.101	-	0.188	-	0.035	-	b
n-pentacosanal	0.047	-	-	-	-	-	-	b
n-Alkanoic Acids								
n-octanoic acid	0.104	0.106	0.122	0.124	0.162	0.131	0.197	a,d
n-nonanoic acid	0.045	0.054	+	+	0.079	0.067	0.109	b,d
n-decanoic acid	0.057	0.087	0.074	0.075	0.078	0.080	0.142	a,d
n-undecanoic acid	0.022	0.050	-	0.017	0.009	0.013	0.012	b,d
n-dodecanoic acid	0.248	0.307	0.287	0.211	0.414	0.299	0.342	a,d
n-tridecanoic acid	0.062	0.071	0.069	0.080	0.078	0.221	0.078	b,d
n-tetradecanoic acid	0.231	0.259	0.325	0.241	0.246	0.440	0.474	a,d
n-pentadecanoic acid	0.224	0.204	0.201	0.200	0.248	0.788	0.582	b,d
n-hexadecanoic acid	2.347	1.926	2.456	2.675	1.032	1.966	5.522	a,d
14-methylhexadecanoic acid	-	-	0.022	0.021	0.382	0.649	0.740	b,d
n-heptadecanoic acid	0.213	0.224	0.232	0.188	0.127	0.361	0.311	b,d
n-octadecanoic acid	0.548	0.606	0.965	0.396	0.315	0.531	2.567	a,d
16-methyloctadecanoic acid	-	-	-	-	0.043	0.065	0.049	b,d
n-nonadecanoic acid	0.087	0.072	0.099	0.080	0.061	0.164	0.108	b,d
n-eicosanoic acid	0.283	0.223	0.375	0.478	0.293	0.600	0.402	a,d
n-heneicosanoic acid	0.299	0.235	0.266	0.192	0.056	0.192	0.059	b,d
n-docosanoic acid	0.899	0.740	1.215	2.252	0.997	3.101	0.341	a,d
n-tricosanoic acid	0.500	0.445	0.361	0.303	0.066	0.216	0.068	b,d

Compound	Hardwoods				Softwoods			Notes
	White Oak	White Oak (Catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (Catalyst)	Loblolly Pine	
n-tetracosanoic acid	2.720	2.171	1.185	1.817	1.505	6.342	0.417	b,d
n-pentacosanoic acid	0.297	0.223	0.193	0.172	0.024	0.084	0.023	b,d
n-hexacosanoic acid	2.246	1.187	0.360	0.469	0.210	1.299	0.080	b,d
n-heptacosanoic acid	0.102	0.067	0.069	0.031	-	-	-	b,d
n-octacosanoic acid	0.146	0.057	0.088	0.051	-	0.024	-	b,d
n-Alkenoic Acids								
hexadecenoic acid	0.263	0.163	0.288	0.191	0.274	0.973	0.325	b,d
cis-9-octadecenoic acid	2.088	2.031	2.488	0.861	0.930	1.302	24.123	a,d
trans-9-octadecenoic acid	0.358	0.270	0.386	0.145	0.211	0.336	1.971	b,d
2-octadecenoic acid	0.105	0.067	0.038	0.084	0.088	0.227	-	b,d
9,12-octadecadienoic acid	2.045	1.946	2.156	1.120	0.774	0.964	2.682	a,d
nonadecenoic acid	0.096	0.078	0.067	0.096	0.022	0.102	-	b,d
eicosenoic acids - 2 isomers	0.185	0.094	0.188	0.166	0.118	0.377	0.309	b,d
heneicosenoic acid	0.110	0.073	0.044	0.051	-	0.055	-	b,d
docosenoic acid	0.318	0.181	0.561	0.453	0.086	0.415	0.022	b,d
tricosenoic acid	0.077	0.047	-	-	-	-	-	b,d
tetracosenoic acid	2.123	0.604	0.262	0.315	-	0.132	-	b,d
pentacosenoic acid	0.294	0.214	0.290	0.232	-	-	-	b,d
hexacosenoic acid	1.517	0.543	-	0.042	-	-	-	b,d
Alkanedioic Acids								
hexanedioic acid	0.269	0.230	0.204	0.302	0.147	0.223	0.317	a,d
heptanedioic acid	0.062	0.088	0.178	0.134	0.062	0.070	0.155	a,d
octanedioic acid	0.119	0.130	0.211	0.329	0.143	0.220	0.350	a,d
nonanedioic acid	0.305	0.263	0.314	0.637	0.302	0.625	0.749	b,d
decanedioic acid	0.097	0.102	0.053	0.106	0.044	0.095	0.113	a,d
hexadecanedioic acid	0.277	0.212	0.298	0.317	0.913	3.559	0.303	b,d
octadecanedioic acid	0.170	0.132	0.110	0.059	0.209	0.751	-	b,d
eicosanedioic acid	0.124	0.113	0.081	0.058	0.094	0.254	0.040	b,d
docosanedioic acid	0.081	0.109	0.343	0.046	0.022	0.133	-	b,d
tetracosanedioic acid	0.218	0.235	0.057	0.019	-	-	-	b,d
pentacosanedioic acid	0.119	0.123	-	-	-	-	-	b,d
hexacosanedioic acid	0.298	0.192	-	-	-	-	-	b,d
heptacosanedioic acid	0.104	0.067	-	-	-	-	-	b,d
Methyl Alkanoates								
methyl hexadecanoate	0.103	0.132	0.085	0.200	0.120	0.079	0.180	a
methyl 14-methylhexadecanoate	-	-	-	-	-	0.021	-	b
methyl heptadecanoate	0.014	0.014	0.013	0.019	0.021	0.020	-	b
methyl octadecanoate	0.030	0.029	0.015	0.033	0.025	0.013	0.047	a
methyl nonadecanoate	0.016	0.012	-	0.010	0.006	0.005	-	b
methyl eicosanoate	0.027	0.025	0.008	0.109	0.014	0.012	0.023	b
methyl heneicosanoate	0.027	0.035	0.009	0.028	-	-	0.015	b
methyl docosanoate	0.079	0.091	0.026	0.948	0.029	0.087	0.024	b
methyl tricosanoate	0.071	0.071	0.016	0.045	-	-	0.016	b
methyl tetracosanoate	0.365	0.341	0.077	0.754	0.028	0.132	0.022	b
methyl pentacosanoate	0.035	0.033	-	0.018	-	-	-	b
methyl hexacosanoate	0.192	0.166	0.008	0.107	0.005	0.016	0.006	b
methyl heptacosanoate	0.019	0.017	-	-	-	-	-	b
Ethyl Alkanoates								
ethyl docosanoate	-	-	-	-	0.024	0.141	-	b
ethyl tetracosanoate	-	-	-	-	0.018	0.079	-	b
Methyl Alkenoates								
methyl cis-9-octadecenoate	0.093	0.062	0.038	0.078	0.032	0.030	0.434	a
methyl 9,12-octadecadienoate	0.055	0.009	0.037	-	0.033	0.041	-	b
methyl eicosenoate	-	-	-	0.048	-	-	-	b
methyl docosenoate	0.055	0.064	-	0.230	-	-	-	b
methyl tetracosenoate	0.321	0.306	0.042	0.107	-	-	-	b

Compound	Hardwoods				Softwoods			Notes
	White Oak	White Oak (Catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (Catalyst)	Loblolly Pine	
methyl hexacosenoate	0.234	0.168	-	-	-	-	-	b
Guaiacol and Substituted Guaiacols								
guaiacol	0.520	0.675	0.699	0.448	0.401	0.231	0.994	a
eugenol	0.175	0.300	0.333	0.350	0.690	0.278	0.523	a
cis-iso-eugenol	0.139	0.120	0.102	0.123	0.197	0.052	0.231	a
trans-iso-eugenol	0.929	0.824	0.476	0.708	0.763	0.397	1.106	b
4-vinylguaiacol	0.681	0.696	0.593	0.545	0.608	0.263	1.055	b
4-ethylguaiacol	0.151	0.133	0.134	0.150	0.841	0.216	0.463	a
4-propylguaiacol	0.051	0.049	0.052	0.058	0.336	0.101	0.146	a
vanillic acid	7.259	8.032	3.688	7.798	8.368	5.463	15.748	a
methyl vanillate	0.271	0.313	0.084	0.134	0.092	0.073	0.283	a
homovanillic acid	33.658	24.437	13.658	18.583	14.108	17.220	90.582	a
methyl homovanillate	0.275	0.185	0.079	0.151	0.091	0.034	0.316	a
vanillin	7.183	6.008	4.934	5.621	7.577	4.802	9.019	a
acetovanillone	6.414	4.376	1.884	3.773	3.919	2.000	7.423	a
propiovanillone	2.514	1.791	0.816	1.537	2.203	0.889	4.596	b
guaiacyl acetone	11.888	7.719	3.654	6.804	15.223	9.835	15.075	b
coniferyl aldehyde	31.410	31.229	33.795	40.325	18.469	27.850	44.690	a
Syringol and Substituted Syringols								
syringol	2.657	2.746	2.305	1.829	0.252	0.040	0.086	a
4-ethylsyringol	7.972	5.148	2.318	2.228	0.964	0.183	0.091	b
4-propylsyringol	4.746	2.764	0.951	2.083	0.720	0.072	0.075	b
methoxyeugenol	11.854	5.952	3.260	5.781	0.731	0.076	0.144	b
cis-methoxy-iso-eugenol	7.473	2.306	0.086	1.791	0.350	0.178	0.716	b
trans-methoxy-iso-eugenol	23.704	6.175	2.442	4.866	0.057	0.032	0.216	b
syringic acid	6.061	4.708	4.055	5.762	-	-	-	a
syringaldehyde	47.108	41.371	49.557	57.058	10.736	5.375	6.508	a
acetosyringone	16.408	12.146	13.687	15.513	2.905	1.655	1.920	a
syringyl acetone	49.293	31.728	28.232	34.752	3.699	1.627	3.311	b
propionyl syringol	3.310	2.507	3.061	3.228	0.828	0.376	0.368	b
sinapyl aldehyde	12.411	11.828	16.065	14.369	0.234	0.655	0.806	a
Other Substituted Benzenes and Phenols								
1,2-benzenediol (pyrocatechol)	29.460	12.018	3.619	5.501	5.810	2.172	5.946	b
1,4-benzenediol (hydroquinone)	1.434	3.641	1.207	3.180	0.691	0.522	1.067	a
1,3-benzenediol (resorcinol)	22.141	7.721	3.822	6.814	3.134	0.987	4.866	a
methyl benzenediols	18.990	9.366	2.600	4.705	3.921	1.579	5.808	b
methoxybenzenediols	15.815	9.469	3.488	3.046	0.362	0.161	0.665	c
hydroxybenzaldehydes	3.937	3.929	1.660	2.957	1.255	0.708	4.025	a
cinnamaldehyde	0.484	0.722	0.937	0.845	1.615	0.466	1.454	b
benzenetriols	1.184	0.076	0.108	0.130	0.298	0.095	0.359	b
hydroxyacetophenones	1.040	1.304	0.666	1.090	1.489	1.048	1.745	b
methyl hydroxybenzoates	0.498	0.362	0.096	0.187	0.088	0.022	0.138	b
trimethoxybenzenes	6.147	4.578	3.030	2.809	0.553	0.043	0.100	b
3,4,5-trimethoxybenzoic acid	9.835	8.125	5.876	3.738	8.312	5.875	-	a
benzoic acid	0.122	0.223	0.230	0.209	0.304	0.220	0.312	a,d
benzene acetic acid	0.193	0.185	0.142	0.137	0.080	0.138	0.129	b,d
benzene propanoic acid	0.094	0.057	0.020	0.037	0.027	0.038	0.041	b,d
Dimers and Lignans								
diguaiacyl ethanes (divanillyls)	1.706	0.790	0.409	0.780	1.814	1.715	3.278	b
syringyl guaiacyl ethane	0.628	2.245	0.142	0.250	-	-	-	b
disyringyl methane	0.097	0.025	0.021	0.024	-	-	-	b
disyringyl ethane	0.767	0.242	0.255	0.283	-	-	-	b
shonanol (2-deoxomatairesinol)	0.289	0.111	0.016	0.025	0.166	0.076	0.328	c
matairesinol	0.006	-	-	-	-	-	-	c

Compound	Hardwoods				Softwoods			Notes
	White Oak	White Oak (Catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (Catalyst)	Loblolly Pine	
PAH and Alkyl PAH								
naphthalene	+	+	+	+	0.066	+	0.063	a
phenanthrene	0.194	0.272	0.561	0.398	0.963	0.598	0.586	a
anthracene	0.032	0.045	0.084	0.054	0.140	0.096	0.092	a
3-methylphenanthrene	0.091	0.062	0.046	0.043	0.058	0.063	0.092	b
2-methylphenanthrene	0.103	0.073	0.055	0.056	0.083	0.112	0.177	b
2-methylanthracene	0.054	0.036	0.025	0.024	0.029	0.033	0.054	a
9-methylphenanthrene	0.089	0.065	0.047	0.050	0.066	0.072	0.094	b
1-methylphenanthrene	0.072	0.054	0.036	0.033	0.079	0.154	0.244	a
phenylnaphthalenes	0.200	0.211	0.144	0.163	0.253	0.719	0.440	b
dimethyl or ethyl 178 MW PAHs	0.215	0.166	0.098	0.103	0.257	0.579	0.652	a
fluoranthene	0.562	0.783	0.746	0.706	1.112	2.200	1.260	a
acephenanthrylene	0.216	0.265	0.261	0.239	0.310	1.035	0.438	b
pyrene	0.552	0.812	0.823	0.719	1.100	2.559	1.339	a
methyl 202 MW PAHs	0.325	0.397	0.433	0.381	0.545	1.337	0.883	b
retene	0.018	0.011	0.008	0.016	1.987	2.594	3.893	a
benzo[ghi]fluoranthene	0.118	0.248	0.296	0.234	0.385	0.763	0.642	b
cyclopenta[cd]pyrene	0.100	0.159	0.150	0.086	0.096	0.602	0.212	b
benz[a]anthracene	0.147	0.272	0.277	0.235	0.351	0.962	0.628	a
chrysene	0.179	0.322	0.340	0.269	0.393	1.084	0.679	a
methyl 226 MW PAHs	0.032	0.063	0.067	0.046	0.065	0.192	0.083	b
methyl 228 MW PAHs	0.049	0.057	0.051	0.043	0.059	0.207	0.095	b
benzo[b]fluoranthene	0.087	0.211	0.183	0.184	0.192	0.457	0.437	a
benzo[k]fluoranthene	0.098	0.227	0.285	0.206	0.276	0.729	0.445	a
benzo[j]fluoranthene	0.043	0.069	0.074	0.058	0.055	0.220	0.103	b
benzo[e]pyrene	0.065	0.132	0.162	0.118	0.146	0.351	0.267	b
benzo[a]pyrene	0.112	0.217	0.253	0.188	0.230	0.673	0.381	a
perylene	0.017	0.030	0.037	0.027	0.029	0.078	0.057	a
indeno[1,2,3-cd]fluoranthene	0.023	0.050	0.051	0.051	0.055	0.133	0.109	b
indeno[1,2,3-cd]pyrene	0.077	0.164	0.191	0.139	0.198	0.450	0.325	a
benzo[ghi]perylene	0.058	0.119	0.138	0.102	0.122	0.271	0.230	a
anthanthrene	0.017	0.021	0.020	0.018	0.014	0.037	0.024	b
dibenz[a,h]anthracene	0.009	0.017	0.016	0.014	0.015	0.044	0.028	a
coronene	0.153	0.240	0.284	0.198	0.183	0.307	0.519	a
Oxy-PAH								
1,4-naphthalenedione	0.032	0.023	0.026	0.019	0.030	0.028	0.024	b
1-naphthol	0.605	0.294	0.082	0.192	0.152	0.158	0.149	a
2-naphthol	0.997	0.647	0.239	0.480	0.570	0.574	0.491	a
methylnaphthols	2.064	1.334	0.553	1.095	1.108	1.192	1.397	b
methoxynaphthols	0.435	0.265	0.098	0.169	0.469	0.355	0.355	a
fluorenone	0.639	0.324	0.377	0.274	0.217	0.378	0.324	a
1-H-phenalen-1-one	0.397	0.427	0.674	0.522	0.523	1.872	0.822	a
9,10-anthracenedione	0.148	0.184	0.229	0.169	0.255	0.512	0.314	a
xanthone	0.107	0.148	0.111	0.095	0.108	0.124	0.151	a
benzanthrone	0.175	0.328	0.439	0.297	0.304	1.180	0.490	a
Sugar Derivatives								
1,4:3,6-dianhydro-α-D-glucopyranose	2.916	2.329	1.940	1.705	2.486	1.222	2.116	c
galactosan	6.548	3.535	3.973	2.552	24.170	11.424	11.450	a
mannosan	5.513	4.131	11.062	12.879	117.654	68.198	46.328	a
levoglucosan	125.144	107.599	213.162	210.067	408.799	396.778	253.106	a
Coumarins and Flavonoids								
coumarin	0.187	0.229	0.260	0.198	0.228	0.156	0.259	a
methoxyhydroxycoumarin	2.418	0.837	-	0.065	-	-	0.097	b
tetramethoxyisoflavone	1.254	0.428	0.218	0.341	-	-	-	b
Furans								
5-hydroxymethyl-2-furaldehyde	9.117	5.409	2.269	7.781	6.549	3.593	8.464	a
5-acetoxymethyl-2-furaldehyde	0.088	0.086	0.164	0.185	0.204	0.069	0.166	a

Compound	Hardwoods				Softwoods			Notes
	White Oak	White Oak (Catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (Catalyst)	Loblolly Pine	
dibenzofuranols	0.447	0.573	0.373	0.472	1.003	1.417	0.981	a
benzonaphthofurans	0.397	0.565	0.506	0.462	0.621	1.002	0.848	c
Resin Acids								
deisopropyldehydroabietic acid	-	-	-	-	0.121	0.122	0.092	b,d
16,17-bisnordehydroabietic acid	-	-	-	-	0.053	0.062	0.052	b,d
16-nordehydroabietic acid	-	-	-	-	0.029	0.030	0.056	b,d
secodehydroabietic acids	-	-	-	-	0.113	0.090	0.159	b,d
pimaric acid	-	-	-	-	0.028	0.057	2.217	a,d
sandaracopimaric acid	-	-	-	-	0.514	0.775	0.477	b,d
dehydroabietic acid	+	+	+	+	5.587	4.424	10.807	a,d
8,15-pimaradien-18-oic acid	-	+	+	-	0.440	0.263	0.194	b,d
isopimaric acid	+	+	+	+	3.012	2.321	0.677	a,d
levo-pimaric acid	+	+	+	+	0.244	0.304	0.233	b,d
abietic acid	-	-	-	-	1.670	3.685	2.810	a,d
7-oxodehydroabietic acid	-	-	-	-	0.321	0.233	0.672	b,d
abieta-6,8,11,13-tetraen-18-oic acid	+	+	+	+	1.659	1.141	2.537	b,d
abieta-8,11,13,15-tetraen-18-oic acid	+	+	+	+	0.266	0.251	0.546	b,d
abieta-6,8,11,13,15-pentaen-18-oic acid	-	-	-	-	0.146	0.138	0.310	b,d
7-oxo-abieta-8,11,13,15-tetraen-18-oic acid	-	-	-	-	0.022	0.018	0.057	b,d
Other Diterpenoids								
19-norabieta-8,11,13-triene	-	-	-	-	0.032	0.021	0.037	b
18-norabieta-8,11,13-triene	-	-	-	-	0.049	0.030	0.050	a
19-norabieta-4,8,11,13-tetraene	-	-	-	-	0.486	0.262	0.290	b
18-norabieta-4(19),8,11,13-tetraene	-	-	-	-	0.173	0.104	0.131	b
dehydroabietane	-	-	-	-	0.022	0.008	-	c
methyl deisopropyldehydroabietate	-	-	-	-	0.006	-	0.018	c
pimarinal	-	-	-	-	-	-	0.047	c
methyl 8,15-pimaradien-18-oate	-	-	-	-	0.018	0.018	-	c
methyl isopimarate	-	-	-	-	0.016	0.034	-	a
methyl 16,17-bisnordehydroabietate	-	-	-	-	0.010	0.011	0.022	c
dehydroabietal	-	-	-	-	0.037	0.033	0.018	c
methyl 6,8,11,13-abietatetraen-18-oate	-	-	-	-	0.158	0.181	0.930	c
methyl 8,11,13,15-abietatetraen-18-oate	-	-	-	-	0.010	0.010	0.118	c
methyl dehydroabietate	-	-	-	-	0.164	0.158	0.852	a
methyl-7-oxodehydroabietate	-	-	-	-	0.054	0.028	0.285	b
juvabione	-	-	-	-	1.040	0.817	0.497	a
todomatuic acid (norjuvabione)	-	-	-	-	3.293	0.518	-	b
Phytosteroids								
stigmasterol	1.101	1.158	1.389	1.470	-	-	0.257	a
β-sitosterol	5.963	3.513	5.864	3.383	1.276	1.155	1.090	a
stigmast-4-en-3-one (sitostenone)	1.721	0.678	0.317	0.072	0.085	0.123	0.091	a
stigmasta-3,5-dien-7-one	0.755	0.452	0.342	0.745	0.238	0.220	0.644	b
stigmasta-4,6-dien-3-one	0.661	0.432	0.174	0.090	0.049	0.125	0.111	b
stigmastan-3-ol	0.379	0.267	0.253	0.241	0.131	-	0.096	a
stigmastan-3-one	1.108	0.649	0.204	0.091	0.034	0.028	0.044	c
Triterpenoids								
friedelin	8.621	6.942	-	-	-	-	-	a
β-amyrone	0.068	0.058	0.005	-	-	-	-	b
β-amyrin	0.144	0.113	0.007	-	-	-	-	a
α-amyrone	0.059	0.041	0.009	-	-	-	-	b
α-amyrin	0.104	0.061	0.013	-	-	-	-	a
Other Compounds								
1-indanone	0.066	0.105	0.141	0.120	0.249	0.070	0.179	a
methyl indanones	0.028	0.025	0.010	0.030	0.072	0.022	0.113	b
squalene	0.107	0.106	0.108	0.090	0.136	0.056	0.547	a
α-tocopherol (vitamin E)	0.772	0.146	-	-	-	-	-	a

Compound	Hardwoods				Softwoods			Notes
	White Oak	White Oak (Catalyst)	Red Maple	Sugar Maple	Douglas Fir	Douglas Fir (Catalyst)	Loblolly Pine	
β -tocopherol	0.131	0.025	-	-	-	-	-	b
unresolved complex mixture (UCM)	563	481	416	452	397	393	664	b

^aIdentification and quantification based on authentic quantitative standard

^bIdentification and quantification based on authentic quantitative standards of compounds with similar structures and retention times

^cIdentification based on relative retention times, mass spectra interpretation, and/or mass spectra libraries, quantification based on TIC response of authentic quantitative standards for other compounds that have similar retention times, functional groups and degree of fragmentation

^dDetected and quantified as methyl ester analog in derivatized fraction

- not detected

+ detected but not quantified due to comparable levels found in blank samples

detected but not quantified due to co-elution of other compounds

Figure 5.2. Organic compound mass balance for the fine particle emissions from the wood stove combustion of U.S. hardwood species

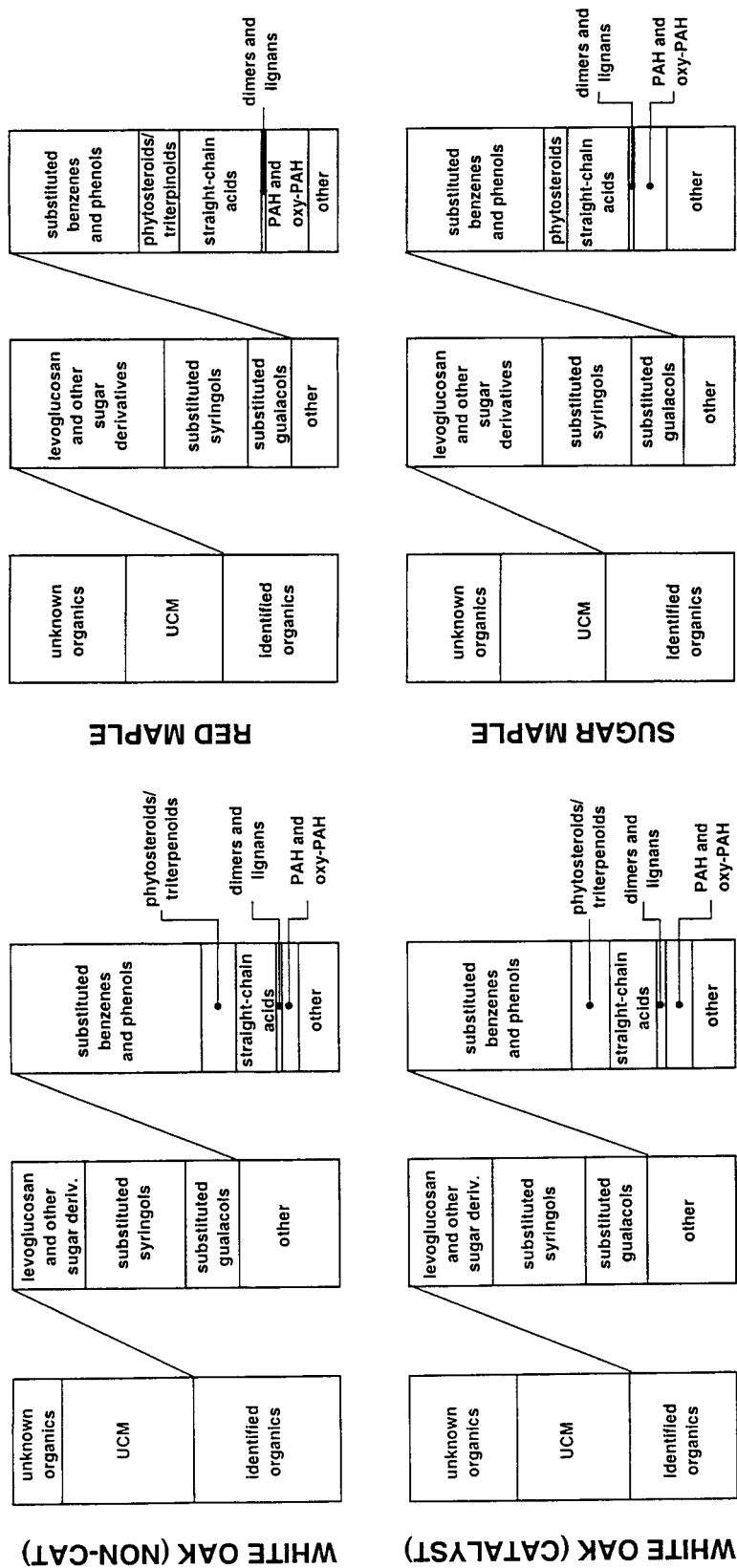
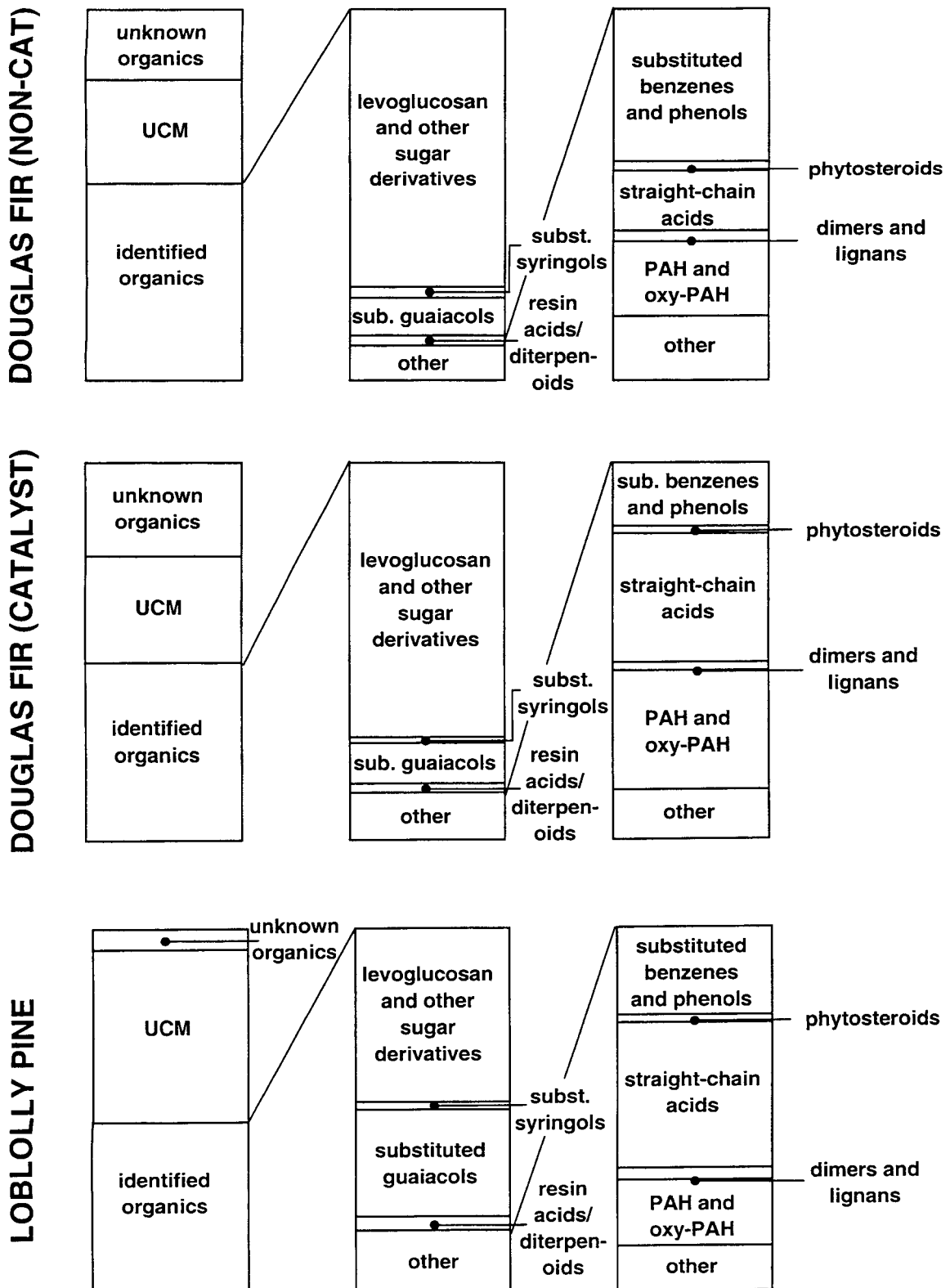


Figure 5.3. Organic compound mass balance for the fine particle emissions from the wood stove combustion of U.S. softwood species



some of these highly polar compounds are not identifiable with our methods, it may explain the higher unidentified organic compound fraction in the fireplace tests. Figures 5.2 and 5.3 also demonstrate some of the previously reported differences between hardwood and softwood combustion that were also found in the fireplace emissions (21-24); the hardwood smoke contains more substituted syringols than the softwood smoke and the resin acids and diterpenoids are only present in softwood smoke.

The general qualitative pattern of individual organic compound emissions shown in Table 5.3 corresponds closely to the results discussed in previous works concerning the same woods burned in a fireplace (21-24). The individual organic compounds that were most abundant in the fireplace smoke are also abundant in wood stove smoke. But when normalized to total organic carbon, organic compounds from wood stove combustion are generally emitted at higher relative levels than the corresponding fireplace test of the same wood species. The increase is, at least in part, due to the absence of additional highly polar compounds that make up the unidentified portion of fireplace smoke. Thus, the normalized emission factors are higher from wood stoves whose emissions contain a lower fraction of unidentified compounds. However, since the overall fine particle mass emission factors per kilogram wood burned are significantly lower for wood stoves, emissions of these compounds on a per kilogram wood burned basis are still generally lower than the emissions from fireplaces.

The triterpenone friedelin, only detected in the smoke from the combustion of white oak in fireplaces (22), was also unique to both catalytic and non-catalytic combustion of white oak in wood stoves. The fraction of total organic carbon quantified as friedelin was higher in the two wood stove tests (8.6 and 6.9 mg/g organic carbon)

than in the corresponding fireplace test (4.4 mg/g organic carbon). Due to the uniqueness of this compound to white oak combustion, friedelin is a promising candidate as a species specific wood smoke tracer. Another molecular tracer for wood combustion, levoglucosan (37), was the most abundant individual organic compound emitted in all fireplace and wood stove tests. Figure 5.4 compares the levoglucosan content of the organic emissions from fireplaces and wood stoves. In general, the levoglucosan content of wood stove emissions is higher than that for fireplace combustion of the same wood species. Across all 22 wood species burned in the fireplace study (21-24), the average levoglucosan emission factor was 129 ± 78 mg/g organic carbon compared to the seven wood stove tests producing an average of 245 ± 114 mg/g organic carbon. If levoglucosan is used as a wood smoke tracer in chemical mass balance receptor models, differences in its emissions between wood stove and fireplace combustion need to be taken into account.

Another important difference between the fireplace, non-catalytic wood stove and catalytic wood stove emissions is seen in the particle-phase emissions of the PAH and alkyl PAH. Figure 5.5 shows that as a fraction of total organic carbon, more PAH compounds are emitted from wood stoves vs. fireplaces when the same wood species is burned. In addition, the catalytic tests resulted in even higher PAH emissions most likely for the same reasons that the elemental carbon emissions were higher for the catalytic tests. As discussed above, the additional pyrolysis that occurs in the catalytic bed can further aromatize the natural wood components into PAH.

The differences between the fine particle organic compound emissions from fireplaces and wood stoves are sufficiently significant to merit separate treatment in

Figure 5.4. Comparison of fine particle mass levoglucosan emissions from the combustion of U.S. wood species in a fireplace, a non-catalytic wood stove, and a catalytic wood stove

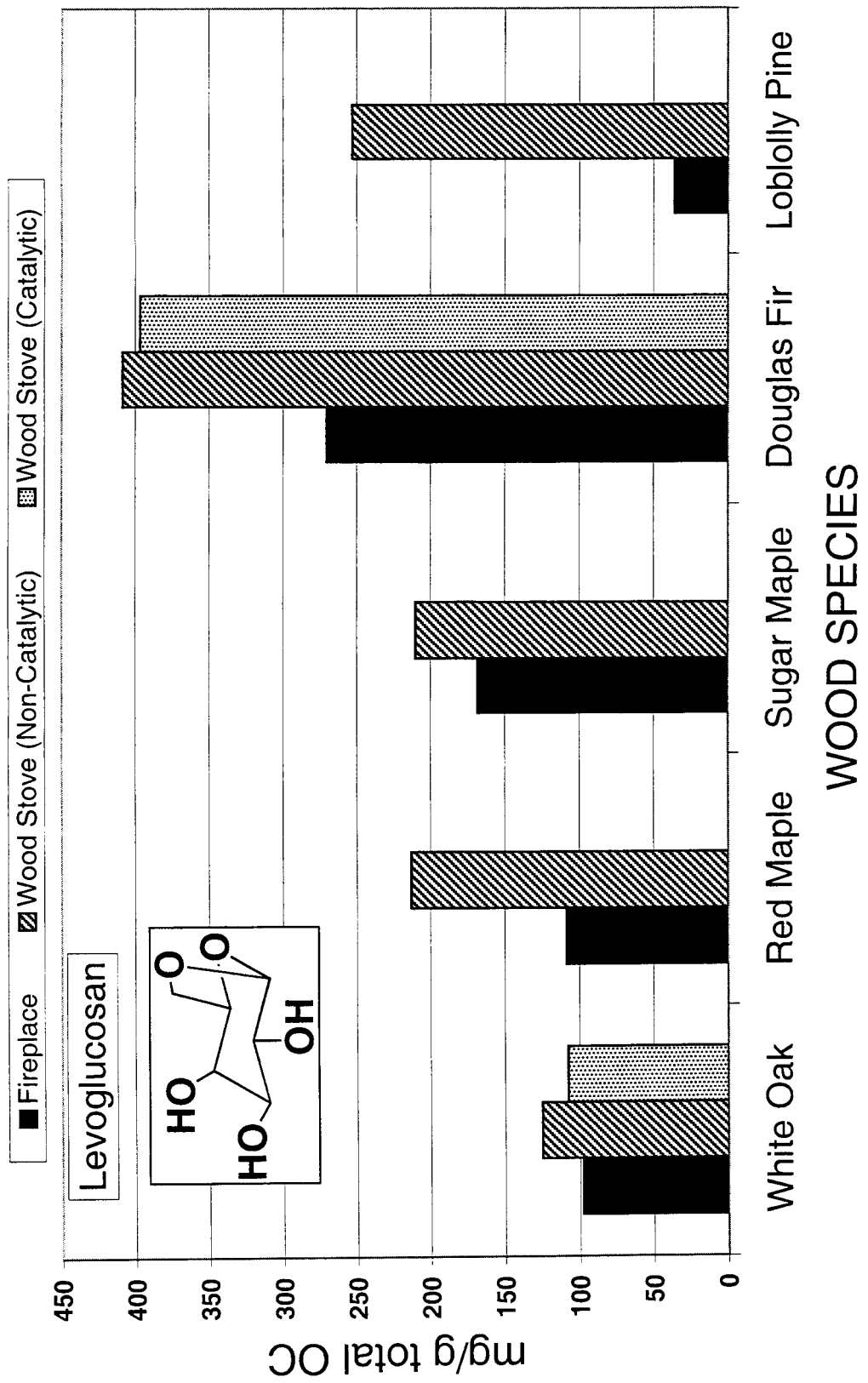
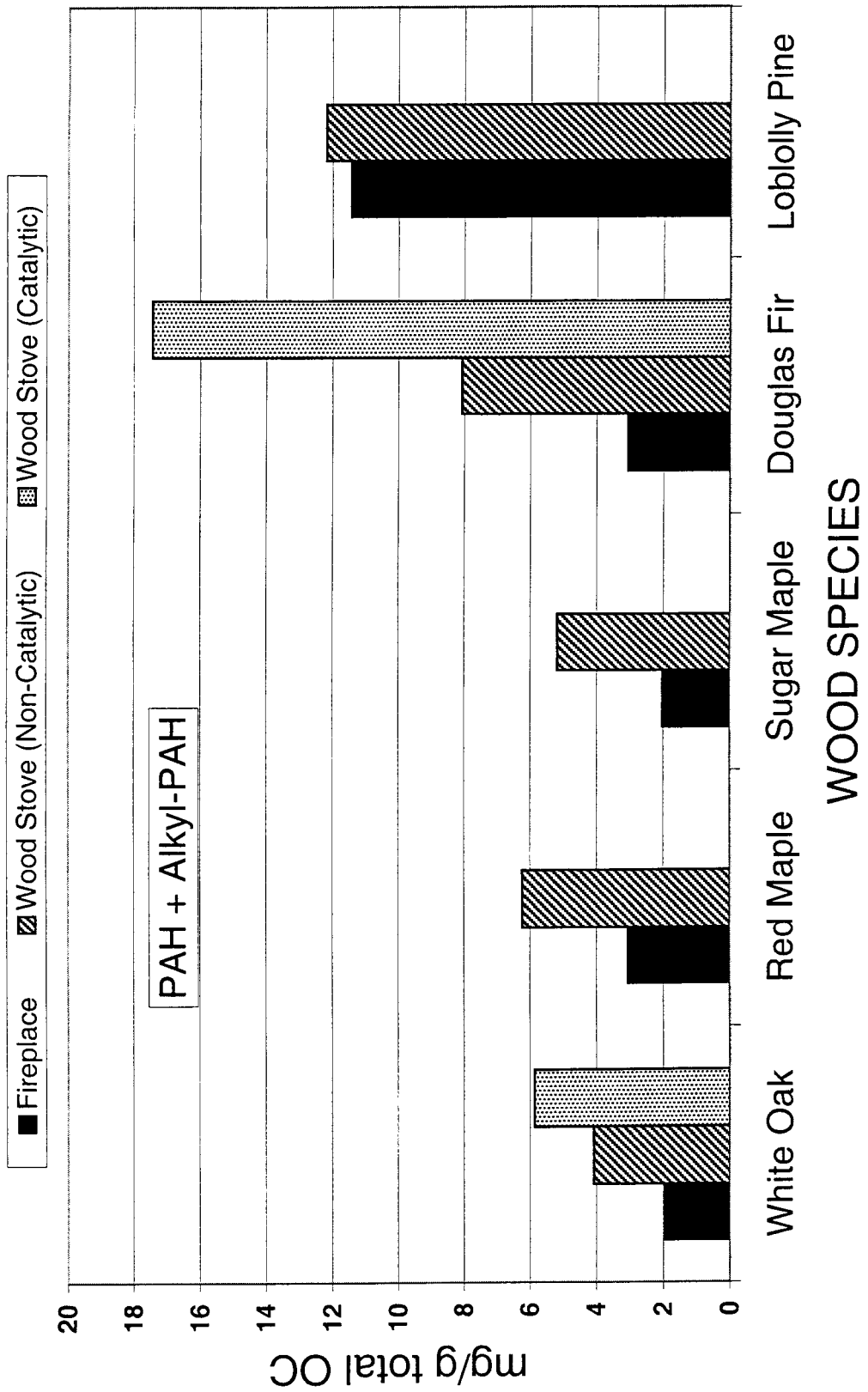


Figure 5.5. Comparison of fine particle PAH and alkyl-PAH emissions from the combustion of U.S. wood species in a fireplace, a non-catalytic wood stove, and a catalytic wood stove



chemical mass balance models that use organic compounds as tracers. It is possible that the contribution to an ambient sample from these two sources cannot be separated by the model calculations due to the similarity of the compounds being emitted. However, one can calculate a weighted composite residential wood combustion source profile based on the wood stove and fireplace usage patterns in a particular region and then use the composite profile for the mass balance calculations.

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Chapter 6

Fine Particulate Organic Compounds Emitted from the Open Burning of Foliar Fuels and Agricultural Wastes

6.1 Introduction

U.S. Environmental Protection Agency (USEPA) emission inventories show that in the year 1995, approximately 10% of non-fugitive dust fine particle emissions in the United States were emitted from the prescribed burning of biomass, with an additional 2% emitted from the open combustion of agricultural wastes (1). Prescribed biomass burning includes the managed burning of foliar fuels to clear land and forest undergrowth, and the open burning of residential waste, with the vast majority of emissions coming from managed burning activities. In certain Southeastern U.S. states such as Georgia, prescribed biomass combustion activities can account for over 80% of the total fine particle biomass combustion emissions (1). Therefore, the particulate emissions from managed and agricultural burning, and any significant differences between the emissions from these sources and other biomass combustion sources such as wood stoves and fireplaces, should be accounted for in regional control strategies aimed at reducing fine particle emissions from biomass combustion.

Source-apportionment techniques using chemical mass balance receptor models have been applied to determine the contributions from the primary particle emissions sources to a particular ambient fine particle sample (2-4). These methods require a detailed chemical characterization of the fine particle mass emitted from each pollution source which is then compared to the chemical composition of a particular ambient sample. While non-mineral potassium and “contemporary” carbon have been used as a

chemical tracers for biomass combustion in general (5-7), these tracers are also emitted by other major sources such as meat cooking (8) and refuse incineration (7, 9). The particle-phase organic compounds emitted from biomass combustion include numerous unique chemical tracers which have previously been used in receptor modeling calculations (2, 3). However, these studies have used fine particle organic source profiles from residential wood combustion to apportion only that biomass combustion source, and have not accounted for emissions from the prescribed combustion of biomass fuels.

Previous studies of emissions from the open burning of foliar fuels and agricultural wastes have focused on gas phase pollutants (10, 11), inorganic species (12), and selected organic compound classes such as PAH (13), and triterpenyl alkanoates (14). However, in order to fully account for prescribed burning emissions in organic compound mass balance models, a full organic speciation, similar to previous studies on residential wood combustion (15-19), is called for. Furthermore, the most important foliar and agricultural fuel types in the United States need to be tested under typical field combustion conditions in order for the results to be applicable to U.S. source-apportionment studies.

The current study analyzes the particulate organic emissions from five prevalent foliar fuel types and two agricultural wastes collected throughout the United States. The prescribed burn fuels consisted of fresh green foliage and litter fall typically consumed in prescribed burn activities such as slash reduction, crowning and low-intensity surface prescribed burns. Such foliar fuels will also burn in uncontrolled wildfires, although under presumably different combustion conditions, and the results may also have some application to wildfire emission characterization. The two agricultural waste types tested

in this study are known to be burned under typical farming practices in some parts of the United States.

6.2 Experimental Methods

6.2.1 Source Tests

The source tests for the burning of the foliar and agricultural fuels were conducted in a test burn facility under the National Risk Management Research Laboratory of the USEPA at Research Triangle Park, North Carolina. All attempts were made to burn the material under the same conditions as it is burned in the field, including fuel mix, fuel moisture content, physical configuration, and air flow characteristics. Controlled combustion of the fuels was performed inside an enclosed burn hut ($\sim 28 \text{ m}^3$) with its interior walls lined with aluminum foil. A ($\sim 2.5 \text{ cm}$) stainless steel pan (0.8 m^2) lined with sand ($\sim 2.5 \text{ cm}$), centrally located on the floor of the burn chamber and positioned on an electronic platform balance, served as the firebox. Mass of the fuels consumed was monitored via remote readout of the balance. The addition of fuel was performed via an inclined ($\sim 40^\circ$) galvanized stainless steel pipe (outside diameter = 30.5 cm, length = 165 cm) and a sealed plunger. A blower delivered unfiltered, ambient combustion air at a fixed velocity, maintaining air circulation and a known mixing ratio in the chamber. Exhaust gas and smoke was extracted from the chamber through a circular duct (outside diameter $\cong 19 \text{ cm}$) located on the wall opposite the air supply fan. A polycarbonate window on a wall of the chamber allowed for visual monitoring of the burning fuel.

A second-generation advanced source sampling system, based on the sampler developed by Hildemann et al. (20), was employed to collect emission samples. The new

sampler improves on the Hildemann design with the addition of automatic flow control, monitoring, and data acquisition. The sampler operates by diluting hot stack emissions with a 25 to 45 fold excess of activated carbon-filtered and HEPA-filtered air. After sufficient residence time and cooling, organic vapors condense onto pre-existing particles yielding a more accurate representation of the partitioning of organic compounds between the gas and particle phases under atmospheric temperatures and concentrations. Smoke samples are withdrawn from the dilution source sampler through an array of cyclone separators operated at the nominal flow required to achieve a 2.5 μm size cut. Teflon filters collected fine particle samples which were weighed to determine gravimetric mass emission factors. Several quartz fiber filters (47 mm diameter, Pallflex tissue quartz 2500 QAO) collect samples which are analyzed for elemental and organic carbon (EC/OC) by thermal evolution/optical transmission methods (21) as well as individual organic compound speciation by gas chromatography/mass spectrometry (GC/MS).

Five foliar fuels and two agricultural waste fuels were selected for testing and are shown in Table 6.1. The tested fuels are described as follows: A Duke Forest leaf litter (*Acer* and *Quercus* sp.) collected from Durham NC; a hemlock pine needle sample (western hemlock-*Tsuga heterophylla*) from Western Oregon; a ponderosa pine needle sample (*Pinus ponderosa*) from Eastern Oregon; a pine/wire grass sample (wiregrass/longleaf pine-*Aristida stricta*/*Pinus palustris*) from Ocala National Forest in Florida; a Fort Bragg pine needle sample (Loblolly pine-*Pinus taeda*) from North Carolina; a rice straw sample from Northern California; and a wheat straw sample from Washington State. Fuel loads ranged between 0.3 and 10 kg/m^2 . All fuels were sealed in

Table 6.1. Fuel moisture content and bulk emission factors for the foliar and agricultural fuels tested

	Forest Litter					Agricultural	
	Duke Forest Leaf Litter	Hemlock Pine Needles	Ponderosa Pine Needles	Ocala Pine/Wire Grass	Fort Bragg Pine Needles	Rice Straw	Wheat Straw
Fuel Moisture Content (%)	13	15	15	<12	14	*	*
Fine Particle Mass Emissions (g/kg burned)	10.8 ± 3.9	11.2 ± 0.7	33.5 ± 10.5	27.2	28.4 ± 11.6	*	4.3
Organic Carbon Emissions (g/kg burned)	8.5 ± 2.9	8.0 ± 0.3	27.8 ± 9.9	19.3	19.7 ± 9.1	*	1.1
Elemental Carbon Emissions (g/kg burned)	0.2 ± 0.01	0.4 ± 0.1	0.4 ± 0.1	0.4	1.3 ± 0.3	*	0.48

* Data not available at time of printing

plastic bags, and stored under refrigerated conditions before use. The gravimetric moisture content of a fuel sub sample (several grams) was determined on the day of testing. All fuel moisture contents, PM_{2.5} mass emission factors, and organic and elemental carbon data shown in Table 6.1 were provided by the team of USEPA researchers and are reported, along with additional data from these tests, in another publication (22). Uncertainties for this data are based on duplicate tests, and uncertainties are omitted when duplicate tests were not performed. The PM_{2.5} mass and the organic and elemental carbon data for the rice straw tests are not yet available.

6.2.2 Organic Chemical Analyses

Organic compound speciation of the wood stove samples was accomplished with procedures similar to those developed by Mazurek et al. (23) and Rogge et al. (24). The methods improve upon the previous methods used for the previous fireplace and wood stove emissions testing (15-19). Briefly, a quartz fiber filter or a portion of a quartz fiber filter is spiked with a mix of deuterated internal recovery standards and then extracted by mild sonication twice in hexane (Fischer Optima Grade) and three times in a benzene/isopropanol mixture (2:1) (benzene: E&M Scientific; isopropanol: Burdick & Jackson). Extracts are filtered, combined, and reduced in volume to approximately 1 ml. The extract is then split and one of the fractions is derivatized with diazomethane to convert organic acids to their methyl ester analogs which are more amenable to GC/MS analysis. The derivatized and underivatized sample fractions are analyzed by GC/MS on a Hewlett-Packard GC/MSD (GC model 5890, MSD model 5973) using a 30 m x 0.25 mm diameter HP-5MS capillary column (Hewlett-Packard) using an auto-injector.

Hundreds of authentic standard mixtures have been prepared for the positive identification and quantification of many of the organic compounds found in ambient particulate matter. These standard suites also contain the same set of internal deuterated standards that were added to our samples. Relative response factors for each compound in the standard mixtures can be calculated relative to an appropriate deuterated compound. These response factors can then be used to quantify each compound in our samples relative to the same internal deuterated compound. When quantitative standards are not available for a given compound or compound class, significant effort is made to obtain a non-quantitative secondary standard that can be used for unique identification of the organic compounds. When a secondary standard is not available, interpretation of mass spectra and mass spectral libraries is used to aid in identification. Quantification of compounds for which primary standards are not available has been estimated from the response factors for compounds having similar retention times, chemical structures, and degrees of fragmentation. Organic speciation results for the two agricultural wastes represent the average of two chemical analyses from two distinct filters collected from the same source test.

6.3 Results

The mass emission factors given in Table 6.1 show that the fine particle mass emissions are generally higher for the prescribed burn fuel than for residential wood combustion (15-19). Residential wood combustion fine particle emission factors range from approximately 1 to 12 grams per kilogram burned while the prescribed burns emit fine particles at levels between 11 and 34 g/kg fuel burned. Similar to the previous

residential wood combustion tests, the majority of fine particle emissions consist of organic carbon with a much smaller elemental carbon component.

Table 6.2 provides the complete organic speciation of the seven fuels tested. Compounds designated by an “a” in the notes column were quantified with authentic quantitative standards. A “b” in the notes column indicates that the compound was quantified with a response factor derived from compounds in the same homologous series or with similar structures. Finally, a “c” indicates that while no good primary or secondary authentic standard exists, identification was based on mass spectra interpretation and libraries and quantification was performed using the total ion response of other compounds with similar retention times, functional groups, and degrees of fragmentation.

The compounds listed in Table 6.2 are grouped by compound class and the results are presented by way of organic compound mass balances in Figures 6.1 – 6.3. Organic carbon results were converted to organic compound mass using a conversion factor of 1.4 to account for the primarily oxygen and hydrogen atoms associated with individual organic compounds (25). Figure 6.1 displays the carbon compound balance for the only primarily hardwood sample, the Duke Forest leaf litter. Approximately 30% of the total organic compound mass was identified and quantified with an additional 13% of the total made up of an unresolved complex mixture of compounds which appear as a large hump underlying the resolved peaks in the gas chromatogram. Sugar derivatives and straight-chain acids are the most prevalent compound classes in the fine particle emissions from this fuel, with smaller amounts of substituted syringols, guaiacols, and phenols.

Table 6.2. Detailed Speciation of Fine Particle Organic Compounds Emitted from Prescribed Burning Activities (all values expressed as mg/g organic carbon (OC) emitted)

Compound	Forest Litter					Agricultural			Notes
	Duke Forest Leaf Litter	Hemlock Pine Needles	Ponderosa Pine Needles	Ocala Pine/Wire Grass	Fort Bragg Pine Needles	Rice Straw	Wheat Straw		
n-Alkanes									
n-octadecane	0.024	-	-	-	0.026	0.015	-	a	
n-nonadecane	0.042	0.081	0.023	0.057	0.046	0.099	0.249	b	
n-eicosane	0.077	0.101	0.022	0.042	0.023	0.061	0.018	a	
n-heneicosane	0.132	0.129	0.028	0.057	0.046	0.113	0.028	b	
n-docosane	0.165	0.109	0.023	0.078	0.065	0.157	0.038	a	
n-tricosane	0.205	0.140	0.045	0.107	0.084	0.184	0.067	b	
n-tetracosane	0.287	0.031	0.027	0.072	0.059	0.235	0.137	a	
n-pentacosane	0.649	0.077	0.029	0.101	0.064	0.272	0.235	b	
n-hexacosane	0.309	0.021	0.014	0.057	0.010	0.266	0.187	b	
n-heptacosane	2.627	#	0.025	0.097	#	0.488	0.878	b	
n-octacosane	0.426	#	#	0.036	#	0.340	0.197	a	
n-nonacosane	13.557	0.064	0.045	0.068	#	1.037	4.726	b	
n-triacontane	0.251	-	-	#	-	0.463	0.130	b	
n-hentriacontane	2.617	-	-	0.099	-	0.949	2.333	b	
n-dotriacontane	0.150	-	-	#	-	0.274	0.048	a	
n-tritriacontane	0.285	-	-	0.073	-	0.351	0.243	b	
n-Alkenes									
1-nonadecene	0.044	0.135	-	0.030	0.039	0.047	#	a	
1-eicosene	0.097	0.226	0.070	0.090	0.049	0.069	0.029	a	
1-heneicosene	0.245	0.132	-	0.080	0.068	0.154	0.046	b	
1-docosene	0.334	0.498	0.066	0.095	0.125	0.295	0.063	b	
1-tricosene	0.415	0.574	0.057	0.143	0.125	0.227	0.094	b	
1-tetracosene	0.926	0.812	0.128	0.482	0.438	0.369	0.207	b	
1-pentacosene	0.603	0.569	-	0.087	0.028	0.251	0.181	b	
1-hexacosene	0.427	0.043	-	0.218	0.135	0.253	0.205	b	
1-heptacosene	0.169	0.194	0.034	0.293	0.158	0.264	0.201	b	
1-octacosene	0.312	-	-	0.084	0.024	0.361	0.405	b	
n-Alkanals									
n-heneicosanal	0.189	-	-	-	-	-	-	b	
n-docosanal	0.134	-	-	0.152	0.134	-	-	b	
n-tricosanal	-	-	-	0.265	0.201	-	-	b	
n-tetracosanal	-	-	-	0.088	0.081	-	-	b	
Alkanoic Acids									
n-octanoic acid	0.168	0.135	0.165	0.129	0.351	0.075	0.071	a,d	
n-nonanoic acid	0.108	0.111	0.164	0.142	0.420	0.073	0.064	b,d	
n-decanoic acid	0.101	0.199	0.149	0.165	0.481	0.089	0.043	a,d	
n-undecanoic acid	0.056	0.418	0.262	0.221	0.485	0.042	0.018	b,d	
n-dodecanoic acid	0.515	7.866	8.945	1.732	5.354	0.611	0.253	a,d	
n-tridecanoic acid	0.164	0.723	0.457	0.504	0.700	0.136	0.041	b,d	
n-tetradecanoic acid	0.992	3.397	4.594	2.133	3.840	0.610	0.663	a,d	
n-pentadecanoic acid	0.353	0.918	0.407	0.668	0.748	0.522	0.200	b,d	
n-hexadecanoic acid	11.083	9.960	13.851	4.878	6.525	12.887	9.294	a,d	
14-methylhexadecanoic acid	-	0.894	0.282	0.038	0.043	0.031	0.011	b,d	
n-heptadecanoic acid	0.532	0.605	0.376	0.294	0.418	0.651	0.194	b,d	
n-octadecanoic acid	2.882	2.850	3.063	1.446	2.049	3.473	1.484	a,d	
16-methyloctadecanoic acid	-	0.183	0.039	-	-	-	-	b,d	
n-nonadecanoic acid	0.307	0.554	0.180	0.189	0.190	0.368	0.086	b,d	
n-eicosanoic acid	2.289	7.195	2.714	1.062	1.197	2.586	0.845	a,d	
n-heneicosanoic acid	1.465	0.763	0.258	0.463	0.386	0.789	0.245	b,d	
n-docosanoic acid	7.667	19.714	4.638	3.075	2.626	2.761	2.005	a,d	
20-methyldocosanoic acid	-	0.064	0.019	-	-	-	-	b,d	
n-tricosanoic acid	3.270	1.901	0.643	1.611	1.342	3.028	0.820	b,d	
n-tetracosanoic acid	14.047	15.629	3.248	11.606	7.026	5.860	1.774	b,d	

Compound	Forest Litter					Agricultural		Notes
	Duke Forest Leaf Litter	Hemlock Pine Needles	Ponder- osa Pine Needles	Ocala Pine/ Wire Grass	Fort Bragg Pine Needles	Rice Straw	Wheat Straw	
n-pentacosanoic acid	1.974	0.618	0.207	0.814	0.591	1.325	0.431	b,d
n-hexacosanoic acid	11.313	1.525	0.402	12.555	5.048	1.941	2.048	b,d
n-heptacosanoic acid	0.893	0.084	0.024	0.158	0.084	0.242	0.285	b,d
n-octacosanoic acid	10.473	0.502	0.110	2.606	0.913	3.715	4.797	b,d
n-nonacosanoic acid	1.698	0.068	-	0.255	0.039	0.513	0.256	b,d
n-triacontanoic acid	18.089	0.920	0.083	1.748	0.182	9.557	3.275	b,d
n-hentriacontanoic acid	0.835	0.073	-	0.195	0.020	0.742	0.070	b,d
n-dotriacontanoic acid	5.822	0.538	0.038	2.267	0.194	9.472	1.375	b,d
n-tritriacontanoic acid	0.281	0.019	-	0.135	0.037	0.574	0.000	b,d
n-tetatriacontanoic acid	1.203	0.200	-	1.423	0.317	3.417	0.136	b,d
n-pentatriacontanoic acid	-	-	-	0.069	0.019	0.093	-	b,d
n-hexatriacontanoic acid	0.043	-	-	0.268	0.086	0.190	-	b,d
Alkenoic Acids								
undecenoic acid	0.022	0.121	0.051	0.067	0.123	0.019	-	b,d
dodecenoic acid	0.046	1.420	1.685	0.515	2.027	-	-	b,d
tridecenoic acid	-	0.067	0.147	0.091	0.085	-	-	b,d
tetradecenoic acid	0.084	1.451	2.574	1.435	2.799	0.027	-	b,d
pentadecenoic acid	0.226	0.523	0.307	0.169	0.336	-	-	b,d
hexadecenoic acid	0.307	4.502	1.777	3.397	4.675	0.386	-	b,d
cis-9-octadecenoic acid	6.182	10.142	25.593	3.758	4.901	10.772	1.532	a,d
trans-9-octadecenoic acid	2.365	1.948	3.858	0.635	1.046	3.986	0.450	b,d
2-octadecenoic acid	0.146	0.273	0.053	0.166	0.157	-	-	b,d
9,12-octadecadienoic acid	4.685	6.300	19.663	2.935	5.206	6.943	2.730	a,d
nonadecenoic acid	0.085	0.061	-	0.018	-	-	0.042	b,d
eicosenoic acid	0.224	1.243	0.065	0.139	-	0.059	0.049	b,d
heneicosenoic acid	0.115	-	0.013	0.042	-	0.025	0.032	b,d
docosenoic acid	1.229	0.514	0.016	0.390	0.304	0.052	0.081	b,d
tricosenoic acid	0.133	0.045	-	0.056	0.050	0.033	0.033	b,d
tetracosenoic acid	0.178	0.139	-	0.929	0.484	0.238	0.058	b,d
pentacosenoic acid	0.097	-	-	-	-	-	-	b,d
hexacosenoic acid	0.532	-	-	0.383	0.129	0.098	0.019	b,d
Alkanedioic Acids								
hexanedioic acid	0.089	0.092	0.084	0.195	0.163	0.081	0.042	a,d
heptanedioic acid	0.095	0.066	0.038	0.149	0.087	0.031	#	a,d
octanedioic acid	0.307	0.231	0.103	0.393	0.251	0.230	0.084	a,d
nonanedioic acid	0.360	0.169	0.076	0.437	0.270	0.347	0.106	b,d
decanedioic acid	0.074	0.046	0.050	0.074	0.038	0.037	0.013	a,d
undecanedioic acid	0.037	0.035	-	0.057	0.084	0.042	0.024	b,d
hexadecanedioic acid	0.244	0.954	0.261	2.372	1.565	0.065	0.027	b,d
octadecanedioic acid	0.141	0.372	0.101	0.581	0.353	0.028	-	b,d
eicosanedioic acid	0.116	1.178	0.145	0.514	0.306	-	-	b,d
docosanedioic acid	0.347	0.472	0.087	0.733	0.499	0.022	-	b,d
tetracosanedioic acid	1.031	0.105	-	0.603	0.289	0.031	-	b,d
pentacosanedioic acid	0.241	-	-	0.028	-	0.025	-	b,d
hexacosanedioic acid	0.086	-	-	0.087	0.013	0.027	-	b,d
Methyl Alkanoates								
methyl pentadecanoate	-	0.045	-	-	-	-	-	b
methyl hexadecanoate	0.234	0.494	0.180	0.065	0.083	0.238	0.047	a
methyl heptadecanoate	0.015	-	0.006	0.006	0.006	0.024	-	b
methyl octadecanoate	0.055	0.092	0.051	0.014	0.018	0.042	0.011	a
methyl nonadecanoate	0.011	0.035	-	-	-	-	-	b
methyl eicosanoate	0.054	0.372	0.038	0.012	0.014	0.052	0.014	b
methyl heneicosanoate	0.091	0.059	-	0.014	0.007	0.024	0.007	b
methyl docosanoate	0.376	1.292	0.127	0.045	0.048	0.076	0.049	b
methyl tricosanoate	0.234	0.126	0.028	0.027	0.023	0.091	0.033	b
methyl tetracosanoate	0.724	0.960	0.093	0.139	0.083	0.175	0.068	b
methyl pentacosanoate	0.069	0.028	0.008	0.010	0.008	0.046	0.024	b
methyl hexacosanoate	0.307	0.102	0.009	0.122	0.053	0.070	0.048	b

Compound	Forest Litter					Agricultural			Notes
	Duke Forest Leaf Litter	Hemlock Pine Needles	Ponderosa Pine Needles	Ocala Pine/Wire Grass	Fort Bragg Pine Needles	Rice Straw	Wheat Straw		
methyl octacosanoate	0.208	0.041	-	0.029	0.011	0.093	0.112	b	
methyl nonacosanoate	0.034	-	-	-	-	0.015	0.010	b	
methyl triacontanoate	0.768	0.214	-	0.032	-	0.403	0.156	b	
methyl hentriacontanoate	-	-	-	-	-	0.037	-	b	
methyl dotriacontanoate	0.209	0.112	-	-	-	0.434	0.097	b	
methyl tetratriacontanoate	-	-	-	-	-	0.150	-	b	
Ethyl Alkanoates									
ethyl docosanoate	-	0.028	0.017	-	-	-	-	b	
ethyl tetracosanoate	0.015	0.023	0.012	0.040	0.014	-	-	b	
ethyl hexacosanoate	0.005	-	-	0.056	0.014	-	-	b	
Methyl Alkenoates									
methyl cis-9-octadecenoate	0.053	0.232	0.209	0.025	0.045	0.103	0.009	a	
methyl trans-9-octadecenoate	0.035	0.103	0.096	0.008	0.018	0.040	0.005	a	
methyl 9,12-octadecadienoate	0.063	0.112	0.121	-	-	0.117	0.022	b	
methyl eicosenoate	0.013	-	-	-	-	-	-	b	
methyl docosenoate	0.112	0.090	-	0.026	-	-	-	b	
methyl tetracosenoate	0.454	0.018	-	0.038	0.012	0.018	-	b	
methyl hexacosenoate	0.030	-	-	0.009	-	0.007	-	b	
Guaiacol and Substituted Guaiacols									
guaiacol	0.176	0.114	0.237	0.506	0.387	0.045	0.034	a	
eugenol	0.015	0.022	0.026	0.036	0.144	0.008	0.011	a	
cis-iso-eugenol	0.011	0.015	0.027	0.056	0.187	0.008	0.005	a	
trans-iso-eugenol	0.072	0.119	0.278	0.604	1.967	0.103	0.058	b	
4-vinylguaiacol	0.209	0.196	0.211	0.504	0.694	0.263	0.158	b	
4-ethylguaiacol	0.026	0.036	0.024	0.044	0.218	0.017	0.014	a	
4-propylguaiacol	0.015	0.022	0.018	0.030	0.129	0.005	0.011	a	
vanillic acid	8.125	5.507	3.970	53.419	29.749	0.790	0.789	a	
methyl vanillate	0.014	0.036	0.012	0.099	0.101	0.004	0.004	a	
homovanillic acid	10.637	45.047	58.9	19.010	26.332	1.677	0.520	a	
methyl homovanillate	0.013	0.018	0.010	0.055	0.039	0.005	-	a	
vanillin	0.272	0.700	0.463	2.328	3.367	0.611	0.248	a	
acetovanillone	0.533	1.232	0.524	3.893	3.959	0.394	0.107	a	
propiovanillone	0.462	0.682	0.219	1.324	1.344	0.086	0.054	b	
guaiacyl acetone	1.321	3.264	1.419	5.714	5.721	0.732	0.303	b	
coniferyl aldehyde	5.862	6.868	1.565	7.838	3.592	-	-	a	
Syringol and Substituted Syringols									
syringol	0.299	0.005	0.003	0.144	-	0.211	0.041	a	
4-ethylsyringol	0.297	0.012	-	0.185	0.009	0.180	0.072	b	
4-propylsyringol	0.278	0.004	-	0.077	-	0.079	0.032	b	
methoxyeugenol	0.653	-	-	0.228	-	0.206	0.076	b	
cis-methoxy-iso-eugenol	0.667	-	-	0.309	-	0.322	0.028	b	
trans-methoxy-iso-eugenol	2.808	-	-	0.781	-	-	-	b	
syringic acid	5.516	-	-	2.952	-	-	-	a	
syringaldehyde	7.480	0.098	-	1.229	-	0.664	0.863	a	
acetosyringone	3.753	0.092	-	0.587	-	1.758	1.437	a	
syringyl acetone	8.268	0.078	-	1.041	0.021	1.177	1.014	b	
propionyl syringol	0.621	0.010	-	0.107	0.016	0.115	0.113	b	
sinapyl aldehyde	4.504	-	-	-	-	-	0.506	a	
Other Substituted Benzenes and Phenols									
1,2-benzenediol (pyrocatechol)	0.186	0.778	2.596	5.513	13.300	1.179	0.060	b	
1,4-benzenediol (hydroquinone)	-	0.023	-	-	-	-	-	a	
1,3-benzenediol (resorcinol)	-	0.514	2.013	1.175	1.101	4.088	0.134	a	
methyl benzenediols	0.149	0.510	0.570	3.204	7.886	0.710	0.104	b	
methoxybenzenediols	-	0.611	0.085	0.607	0.674	0.371	0.095	c	
hydroxybenzaldehydes	0.271	0.510	0.270	0.746	0.525	0.690	0.272	a	
benzenetriols	-	-	-	0.863	0.702	-	-	b	

Compound	Forest Litter					Agricultural		Notes
	Duke Forest Leaf Litter	Hemlock Pine Needles	Ponder- osa Pine Needles	Ocala Pine/ Wire Grass	Fort Bragg Pine Needles	Rice Straw	Wheat Straw	
hydroxyacetophenones	0.317	0.521	0.340	0.852	0.858	0.474	0.332	b
methyl hydroxybenzoates	0.015	0.133	0.369	0.013	0.028	0.014	0.007	b
trimethoxybenzenes	0.216	0.011	0.002	0.288	-	0.141	0.050	b
3,4,5-trimethoxybenzoic acid	67.003	-	-	3.599	-	4.451	3.157	a
benzoic acid	0.153	0.185	0.619	0.168	0.587	0.139	0.156	a,d
benzene acetic acid	0.087	0.094	0.152	0.122	0.430	0.112	0.132	b,d
benzene propanoic acid	0.042	0.126	0.212	0.090	0.215	0.111	0.047	b,d
Dimers and Lignans								
diguaiacyl ethanes (divanillyls)	0.580	1.315	0.491	1.009	1.617	0.164	0.183	b
syringyl guaiacyl ethane	0.208	-	-	0.030	-	0.033	0.040	b
disyringyl methane	0.032	-	-	0.014	-	0.053	0.023	b
disyringyl ethane	0.264	-	-	0.027	0.005	0.011	0.033	b
shonanin (2-deoxomatairesinol)	0.161	0.476	0.269	0.366	0.435	0.006	0.017	c
methyl-2-deoxomatairesinol	-	0.011	0.004	0.004	0.004	-	-	c
matairesinol	-	0.053	0.113	0.031	0.050	-	-	c
PAH and Alkyl PAH								
naphthalene	0.016	0.012	0.010	0.011	0.009	0.013	0.022	a
phenanthrene	0.007	0.029	0.038	0.027	0.097	0.031	0.019	a
anthracene	0.001	0.005	0.007	0.003	0.013	0.007	0.005	a
3-methylphenanthrene	0.007	0.033	0.019	0.014	0.043	0.023	0.012	b
2-methylphenanthrene	0.008	0.089	0.063	0.043	0.134	0.044	0.019	b
2-methylanthracene	0.008	0.024	0.021	0.012	0.029	0.037	0.022	a
9-methylphenanthrene	0.009	0.060	0.034	0.030	0.120	0.036	0.012	b
1-methylphenanthrene	0.005	0.173	0.090	0.099	0.355	0.040	0.009	a
phenylnaphthalenes	0.023	0.046	0.026	0.018	0.035	0.028	0.024	b
dimethyl or ethyl 178 MW PAHs	0.045	0.663	0.499	0.460	0.992	0.116	0.039	a
fluoranthene	0.034	0.037	0.026	0.028	0.053	0.068	0.123	a
acephenanthrylene	0.011	0.009	0.012	0.008	0.013	0.010	0.040	b
pyrene	0.043	0.043	0.048	0.027	0.047	0.061	0.124	a
methyl 202 MW PAHs	0.046	0.091	0.054	0.055	0.092	0.127	0.175	b
retene	0.041	4.388	1.097	1.799	4.282	0.101	0.009	a
benzo[ghi]fluoranthene	0.008	0.010	0.007	0.008	0.010	0.014	0.074	b
cyclopenta[cd]pyrene	0.003	0.002	0.002	0.001	0.001	0.002	0.017	b
benz[a]anthracene	0.017	0.017	0.012	0.011	0.018	0.042	0.159	a
chrysene	0.020	0.025	0.017	0.013	0.024	0.037	0.160	a
methyl 226 MW PAHs	0.002	-	0.001	-	-	0.007	0.033	b
methyl 228 MW PAHs	0.013	0.016	0.007	0.010	0.016	0.023	0.067	b
benzo[b]fluoranthene	0.009	0.009	0.006	0.005	0.009	0.027	0.122	a
benzo[k]fluoranthene	0.007	0.007	0.005	0.006	0.009	0.020	0.123	a
benzo[j]fluoranthene	0.002	0.002	0.001	0.002	0.002	0.008	0.036	b
benzo[e]pyrene	0.061	0.008	0.004	0.006	0.006	0.017	0.093	b
benzo[a]pyrene	0.012	0.009	0.006	0.007	0.010	0.033	0.162	a
perylene	0.001	0.001	0.001	0.002	0.002	0.003	0.013	a
indeno[1,2,3-cd]fluoranthene	0.010	0.002	0.001	0.002	0.002	0.004	0.033	b
indeno[1,2,3-cd]pyrene	0.006	0.005	0.003	0.004	0.005	0.017	0.096	a
benzo[ghi]perylene	0.006	0.004	0.003	0.004	0.005	0.016	0.096	a
anthanthrene	0.002	-	0.000	-	-	0.002	0.011	b
dibenz[a,h]anthracene	0.001	0.001	-	0.001	0.001	0.002	0.011	a
coronene	0.011	0.033	0.012	-	-	-	0.114	a
Oxy-PAH								
1-naphthol	0.033	0.076	0.047	0.054	0.181	0.191	0.043	a
2-naphthol	0.097	0.242	0.119	0.165	0.283	0.331	0.225	a
methylnaphthols	0.429	0.809	0.391	0.702	1.002	1.373	0.618	b
fluorenone	0.036	0.085	0.106	0.019	0.032	0.035	0.018	a
1-H-phenalen-1-one	0.059	0.033	0.018	0.014	0.025	0.070	0.191	a
9,10-anthracenedione	0.014	-	-	-	-	-	0.033	a
xanthone	0.007	0.020	0.006	0.004	-	0.009	0.009	a
benzanthrone	0.045	0.052	0.036	0.030	0.032	0.067	0.769	a

Compound	Forest Litter					Agricultural		Notes
	Duke Forest Leaf Litter	Hemlock Pine Needles	Ponder-osa Pine Needles	Ocala Pine/Wire Grass	Fort Bragg Pine Needles	Rice Straw	Wheat Straw	
Sugar Derivatives								
1,4:3,6-dianhydro- α -D-glucopyranose	0.148	0.435	0.616	2.068	3.315	1.397	0.355	c
galactosan	0.398	5.794	2.770	0.468	6.755	-	-	a
mannosan	5.922	17.472	9.334	7.792	10.999	-	-	a
levoglucosan	93.6	59.1	33.2	148.0	121.0	126.5	100.0	a
monomethyl inositol	-	8.947	7.240	-	3.424	-	-	c
Coumarins and Flavonoids								
tetramethoxyisoflavone	0.533	-	-	0.171	-	0.427	0.606	b
Furans								
5-hydroxymethyl-2-furaldehyde	1.301	2.206	2.928	25.487	39.811	3.319	0.272	a
dibenzofuranols	0.050	0.091	0.090	0.061	0.084	0.137	0.220	a
benzonaphthofurans	0.028	0.073	0.038	0.026	0.051	0.044	0.069	c
Resin Acids								
deisopropyldehydroabietic acid	0.003	0.136	0.064	0.060	0.395	0.007	0.006	b,d
16,17-bisnordehydroabietic acid	-	0.046	0.024	0.095	0.147	-	-	b,d
16-nordehydroabietic acid	0.002	0.069	0.030	0.201	0.418	0.001	0.002	b,d
secodehydroabietic acids	0.012	0.389	0.296	0.334	1.442	-	0.013	b,d
pimaric acid	0.003	0.920	0.495	1.245	1.841	-	0.019	a,d
sandaracopimaric acid	0.009	1.039	0.526	0.698	1.575	-	0.018	b,d
dehydroabietic acid	0.096	5.496	5.939	5.422	6.078	0.067	0.226	a,d
8,15-pimaradien-18-oic acid	0.033	1.375	0.476	0.722	1.729	-	-	b,d
isopimaric acid	0.225	3.923	8.011	2.409	5.942	0.268	0.060	a,d
levo-pimaric acid	0.008	3.193	1.881	0.990	6.147	0.066	0.033	b,d
abietic acid	0.256	41.626	28.001	14.708	61.034	0.132	-	a,d
7-oxodehydroabietic acid	0.006	0.251	0.184	1.151	1.341	0.001	0.004	b,d
abieta-6,8,11,13-tetraen-18-oic acid	0.026	1.877	1.161	4.608	4.296	0.008	0.032	b,d
abieta-8,11,13,15-tetraen-18-oic acid	0.008	0.390	0.386	1.147	1.955	0.002	0.002	b,d
abieta-6,8,11,13,15-pentaen-18-oic acid	0.005	0.185	0.211	0.857	1.089	-	-	b,d
neoabietic acid	0.008	0.305	1.130	0.250	1.989	-	-	b,d
7-oxo-abieta-8,11,13,15-tetraen-18-oic acid	0.004	0.024	0.024	0.148	0.165	-	-	b,d
Other Diterpenoids								
19-norabieta-8,11,13-triene	-	0.095	0.048	0.047	0.365	-	-	b
18-norabieta-8,11,13-triene	-	0.196	0.090	0.094	0.658	0.002	-	a
19-norabieta-4,8,11,13-tetraene	0.003	0.395	0.197	0.225	0.842	-	0.004	b
18-norabieta-4(19),8,11,13-tetraene	-	0.212	0.102	0.073	0.249	-	0.001	b
dehydroabietane	-	0.037	0.005	0.011	0.062	0.001	-	c
methyl deisopropyldehydroabietate	-	0.013	0.004	0.005	0.021	-	-	c
pimarinal	-	0.149	-	-	0.027	-	-	c
methyl 8,15-pimaradien-18-oate	-	0.116	0.019	0.012	0.028	-	-	c
methyl isopimarate	-	0.431	0.129	0.023	0.171	-	-	a
methyl 16,17-bisnordehydroabietate	-	0.010	0.003	0.007	0.011	-	-	c
dehydroabietal	-	0.057	0.009	0.003	0.014	-	-	c
methyl 6,8,11,13-abietatetraen-18-oate	0.004	0.285	0.071	0.206	0.399	0.004	-	c
methyl 8,11,13,15-abietatetraen-18-oate	0.001	0.064	0.061	0.118	0.214	0.001	-	c
methyl dehydroabietate	0.006	0.760	0.180	0.291	0.811	0.014	0.009	a
methyl abietate	-	0.817	0.350	0.288	1.394	0.046	-	a
methyl-7-oxodehydroabietate	0.001	0.071	0.018	0.114	0.122	0.001	0.002	b
manoyl oxide	-	-	-	0.285	0.734	-	-	b
manool	-	17.250	-	-	-	-	-	a
juvabione	-	-	-	0.078	0.078	-	-	a
Phytosteroids								
stigmasterol	-	-	-	-	-	5.362	1.648	a
β -sitosterol	5.373	10.558	4.497	3.119	4.046	5.258	8.786	a
stigmast-4-en-3-one (sitostenone)	0.727	1.087	0.162	1.549	0.737	0.264	0.189	a
stigmasta-3,5-dien-7-one	0.176	0.260	0.113	0.407	0.215	0.505	0.269	b

Compound	Forest Litter					Agricultural		Notes
	Duke Forest Leaf Litter	Hemlock Pine Needles	Ponderosa Pine Needles	Ocala Pine/Wire Grass	Fort Bragg Pine Needles	Rice Straw	Wheat Straw	
stigmasta-4,6-dien-3-one	0.143	0.225	0.036	0.198	0.089	0.033	0.055	b
stigmastan-3-ol	0.098	0.072	-	0.054	-	0.190	0.240	a
stigmastan-3-one	0.087	0.050	0.005	0.089	0.018	0.032	0.007	c
Triterpenoids								
friedelin	0.180	-	-	-	-	-	-	a
β -amyrone	0.303	-	-	0.018	-	-	0.007	b
β -amyrin	0.700	-	-	0.044	-	-	0.063	a
α -amyrone	0.561	-	-	0.027	-	-	0.006	b
α -amyrin	1.040	-	-	0.060	-	-	0.041	a
Other Compounds								
1-indanone	0.009	0.012	0.011	0.008	0.040	0.016	0.016	a
methyl indanones	-	0.007	0.005	0.009	0.039	-	0.010	b
squalene	1.583	0.409	0.557	0.524	0.181	0.274	0.408	a
α -tocopherol (vitamin E)	18.610	1.557	3.342	2.978	2.016	2.331	0.632	a
δ -tocopherol	4.601	-	-	0.213	-	0.061	0.016	a
β -tocopherol	3.622	0.014	0.019	0.132	0.019	0.100	0.021	b
γ -tocopherol	3.416	0.075	0.045	0.291	0.127	0.806	0.090	b
unresolved complex mixture (UCM)	176	305	131	290	376	376	265	b

^aIdentification and quantification based on authentic quantitative standard

^bIdentification and quantification based on authentic quantitative standards of compounds with similar structures and retention times

^cIdentification based on relative retention times, mass spectra interpretation, and/or mass spectra libraries, quantification based on TIC response of authentic quantitative standards for other compounds that have similar retention times, functional groups and degree of fragmentation

^dDetected and quantified as methyl ester analog in derivatized fraction

- not detected

detected but not quantified due to co-elution of other compounds

Figure 6.1. Organic compound mass balance for the fine particle emissions from the open burning of a Duke Forest leaf litter

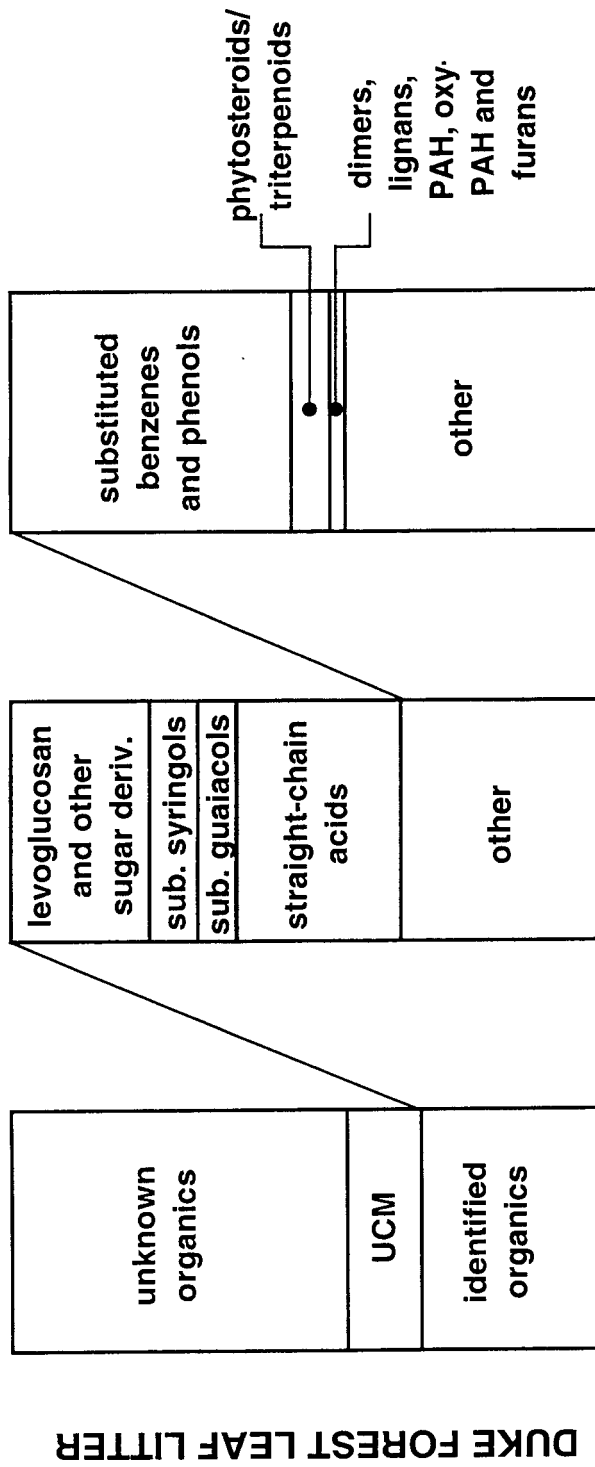


Figure 6.2 gives the carbon compound mass balances for the fine particle emissions from the four primarily softwood forest litters. Between 21% and 34% of the total carbon compound mass was identified and quantified in these samples. Sugar derivatives, including levoglucosan, are major components of the fine particle emissions as was the case for the one hardwood litter. However, substituted syringols are not present, with the exception of a small amount in the Ocala pine/wire grass sample. A similar result has been seen in the previous residential wood combustion tests where it was found that only the hardwood species emit appreciable amounts of the syringol compounds (15-19). The syringols in the Ocala sample most likely came from the grass component or possible inclusion of some hardwood detritus in the litter mix. Another difference between the hardwood litter emissions and the four softwood fuels are the large resin acid and diterpenoid component. This result is also consistent with the residential wood burning results which found the same hardwood/softwood distinction with respect to this compound class (15-19). More furans, PAH and oxy-PAH are also associated with these four softwood litters than with the hardwood sample.

The results for the carbon compound mass balance of the agricultural waste combustion fine particle emissions is given in Figure 6.3. A smaller fraction of the total organic compound mass (12%-19%) was identified and quantified, most likely due to the presence of novel compounds unique to these fuel types for which standards have not been developed. Levoglucosan and other sugar derivatives are the predominant compound class identified, with lower levels of the substituted guaiacols, syringols, and phenols than were seen in the other prescribed burning fuels.

Figure 6.2. Organic compound mass balance for the fine particle emissions from the open burning of primarily softwood forest litters

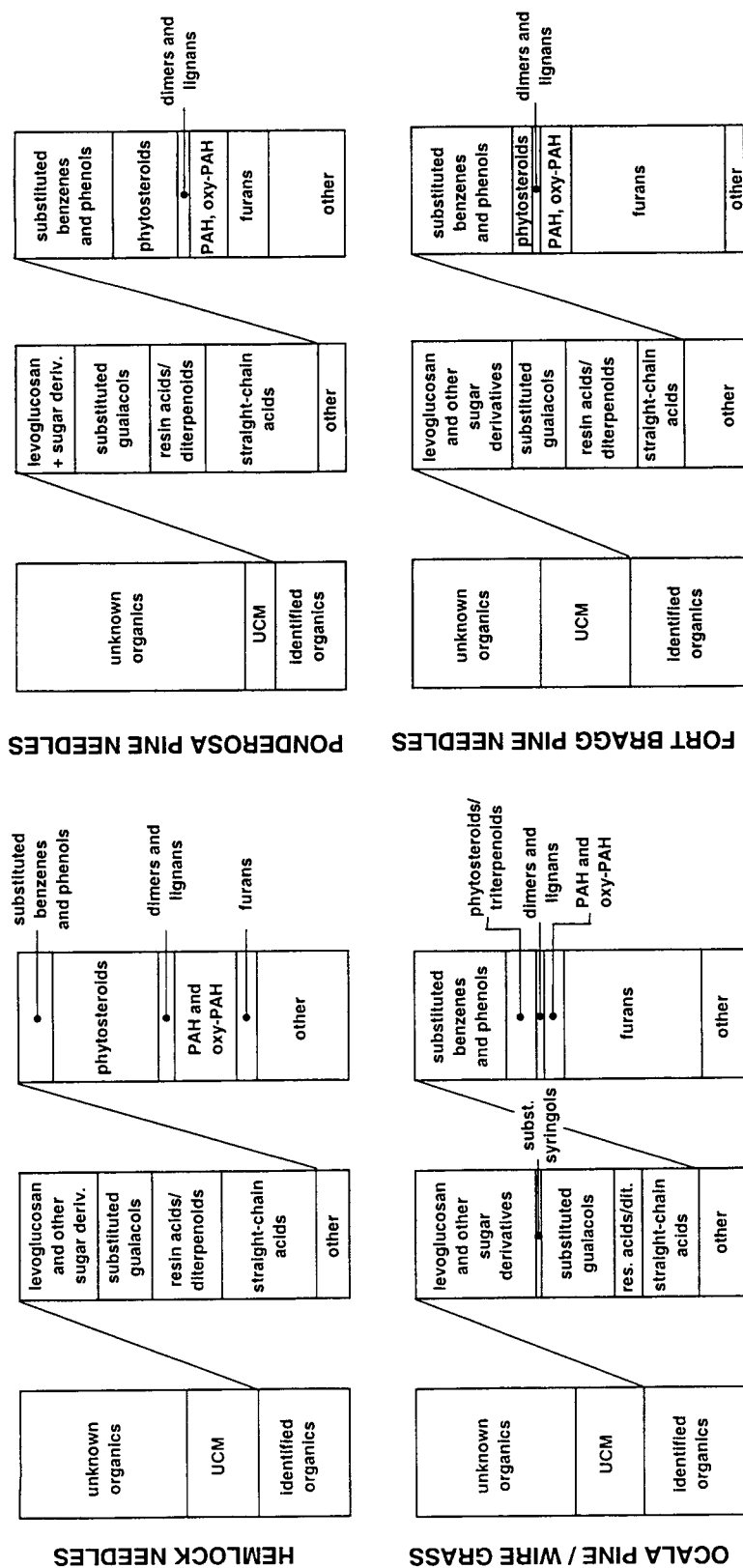
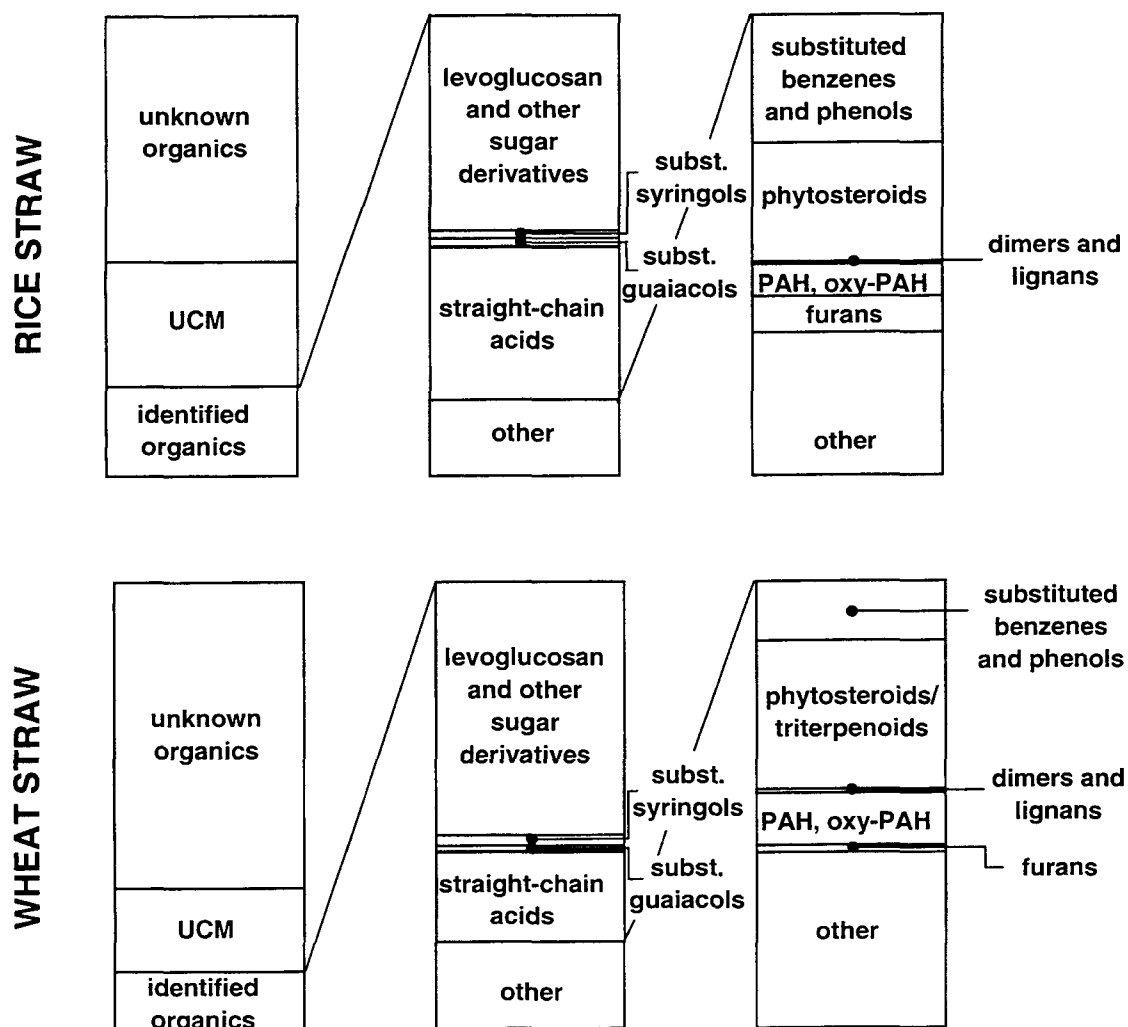


Figure 6.3. Organic compound mass balance for the fine particle emissions from the open burning of agricultural wastes



In general, the carbon compound mass balances show similar results to those found in the fine particle emissions from residential wood combustion (15-19). The foliar and agricultural fuels tend to emit more straight-chain acids than the wood combustion since more plant waxes which contain these compounds are present in the foliage of trees than in the wood or bark. In most cases, more PAH, oxy-PAH, and furans were emitted from the prescribed burning fuels than in the residential wood combustion fuels.

A more detailed investigation of the individual organic compounds found in the fine particle emissions from these fuels, as given in Table 6.2, reveals additional variations in the emissions profiles. All values in the table are normalized to total fine particle organic carbon emitted. The n-alkane emissions follow more of the odd-carbon number preference than was found in many of the residential wood combustion tests (15-19), and extend to higher carbon numbers. Again, this is most likely due to the plant waxes located in the foliar portions of the trees. An unusually high level of n-nonacosane was found in the Duke Forest litter and the wheat straw relative to the other fuels. Very low levels of n-alkenes and n-alkanals were detected in the fine particle emissions from all the prescribed and agricultural fuel combustion tests.

Also due to the higher plant wax component of these foliar fuels, the levels of alkanoic acids measured were generally higher than the residential wood combustion tests (15-19). The alkanoic acids exhibit the well known even carbon number preference of natural materials (26). The predominant alkanoic acid emitted differed from fuel to fuel with generally heavier alkanoic acids emitted from the hardwood and agricultural fuel combustion. Like the residential wood combustion tests (15-19), the most prevalent

alkenoic acids were *cis*-9-octadecenoic acid and 9,12-octadecadienoic acid. The Ponderosa pine needles showed particularly high levels of these two compounds.

As noted above, the combustion of softwood litters produced more substituted guaiacol emissions than the hardwood litter or the agricultural fuels. The dominant compounds in this class were homovanillic acid, vanillic acid, and coniferyl aldehyde. The agricultural fuels, which can both be classified as types of grasses and are neither hardwoods nor softwoods, emit less substituted guaiacols when burned. With the exception of the Ocala sample, which may have included some hardwood or grass species, the softwood litter smokes contain much less substituted syringol material than the hardwood litter smoke. However, the agricultural waste combustion emissions did contain appreciable quantities of compounds in this class. 3,4,5-Trimethoxybenzene was found at very high levels in the Duke Forest sample relative to the other fuels burned.

Like the residential wood combustion tests (15-19), PAH and oxy-PAH are not major components of the fine particle emissions from the combustion of these fuels. The exception is the high level of retene found in the softwood litter smokes, which is also found in high quantities in the softwood combustion in wood stoves and fireplaces. Retene is expected in softwood smoke since it is a thermal alteration product of the resin acids present in conifer woods.

The anhydrous sugar, levoglucosan, has recently been used as a good general biomass combustion tracer (3). It is generally the single most abundant compound in biomass smoke from residential wood combustion and the current results for the foliar and agricultural fuels are no different. Between 33 and 148 mg per g organic carbon were measured in the foliar burn smokes. The agricultural waste combustion also yields

levoglucosan levels in this range. The range also corresponds with the range found in the residential wood combustion tests (15-19). Therefore, levoglucosan remains a good biomarker for biomass combustion in general since emission factors seem to be relatively consistent across fuel types and burn conditions.

As expected, resin acids were found at much higher levels in the softwood litter smokes than in the hardwood or agricultural smokes. The dominant resin acid was abietic acid, with lesser amounts of dehydroabietic acid, isopimaric acid, and abieta-6,8,11,13-tetraen-18-oic acid. A very high level of manool was quantified in the Hemlock needle sample and was not found above detection limits in any of the other fuel samples tested here. As was the case in the residential wood combustion results (15-19), the most abundant phytosteroid was β -sitosterol, which was emitted in significant quantities from all of the fuel types tested. The combustion of the agricultural wastes produced more particle-phase stigmasterol than the combustion of the foliar fuels. The tocopherol compounds, including vitamin E, were present in the Duke Forest litter smoke in much higher quantities than in any of the other fuel smokes.

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Chapter 7

Organic Compounds in Biomass Smoke from Residential Wood Combustion: Emissions Characterization at a Continental Scale

7.1 Introduction

Assessing the contribution of residential wood combustion to ambient fine particle concentrations presents a difficult challenge for environmental scientists and policy-makers for a variety of reasons. Residential wood burning activity can vary significantly from region to region and from season to season. The amount of wood being burned can also vary on a daily or hourly basis depending on outdoor temperatures and the day of the week. The types of woods being burned also depend on region and can produce different fine particle emission factors (1-7). Different wood combustion appliances, including wood stoves, fireplaces and any corresponding emissions control equipment, can lead to very different emission characteristics even when the same woods are burned (3, 8, 9). Other factors such as fuel moisture content, burn rate, log size and log configuration also can significantly effect emission factors (8-11). Currently, the best estimates of the amount of fine particulate matter emitted to the atmosphere from residential wood combustion are based on emissions inventory approaches. According to the U. S. Environmental Protection Agency (USEPA) 34% of the total non-fugitive dust $PM_{2.5}$ emissions in the United States during calendar year 1995 came from biomass combustion sources, with 36% of that figure coming from residential wood combustion (12). However, these annual emissions estimates do not help in determining the contribution of residential wood combustion fine particle emissions to specific pollution

events which instead tend to reflect day to day variations in home heating demand as well as meteorological conditions.

Instead of estimating the relative importance of wood smoke based on emissions inventory calculations, chemical mass balance receptor models can be used to determine the fraction of ambient fine particle mass attributable to a particular source (13-15). By comparing detailed fine particle organic chemical composition data from emissions source tests with the corresponding chemical composition of ambient fine particle samples, a nearly complete source apportionment of the atmospheric fine particle burden can be achieved. These methods require the use of unique particle phase chemical markers or source signatures to effectively trace emissions from a particular source. For biomass combustion sources such as residential wood combustion, non-soil potassium has been proposed as a wood smoke marker (16). However, particulate potassium has other emission sources, such as meat cooking (17) and refuse incineration (18, 19), which complicate its use as a wood smoke tracer. Isotopically "modern" carbon has also been used as a biomass combustion marker (19, 20) but this too has other sources such as food cooking, cigarette smoking, and the abrasion products from leaf surfaces (21). A better source of possible wood smoke tracers can be found in the over 250 individual organic compounds previously identified in wood smoke (1-7, 22, 23). Potential marker compounds include substituted phenols, resin acids, and certain phytosteroids, all of which are relatively unique to biomass combustion.

The use of organic compounds as tracers in chemical mass balance receptor models has been successfully demonstrated at specific locales in California. Over a three day period in Fresno, California, in 1995, over 50% of the ambient fine particle

concentration was demonstrated to be due to wood combustion using these methods (14). Another chemical mass balance calculation using organic compounds determined that for a 1982 annual average in Southern California, up to 10% of the ambient fine particle mass consisted of wood smoke (13). However, if these methods are to be applied at a national scale, source chemical composition profiles which reflect regional differences in wood types and appliance use may be necessary. At the present time, the extent of region-to-region differences in wood smoke composition in North America is completely unknown.

It has already been shown that different wood species and different combustion appliances can produce different mass emission factors and organic compound source signatures (2-7). Hardwood combustion emits significantly more substituted syringol compounds than softwood combustion and resin acids are emitted only from the burning of softwoods. The emission factors of certain phytosterols, such as β -sitosterol, can vary greatly with wood species (2, 4-7). Other organic species, such as betulin, friedelin, juvabione and yangambin may be unique to a particular wood species or class (2, 4, 5). Furthermore, although wood stoves and fireplaces emit similar compounds when burning the same wood type, the relative amounts of these compounds can differ as combustion parameters are changed. A single residential wood combustion organic compound source profile might not be applicable for use across North America because wood species availability and appliance ownership vary regionally.

To quantify the extent of regional variations in wood smoke organic chemical composition, an extensive series of source tests was conducted while burning the most available wood species in the United States (2, 4-7). The methods for selecting the wood

species, conducting the source tests, and analyzing the particulate emissions have been reported previously (2). Twenty-two wood species were burned in a conventional masonry home fireplace and five of these species were also tested in a wood stove operated with no emission control technology. The resulting source organic chemical composition profiles for individual wood species burned in both fireplaces and wood stoves are also given in the previous publications cited above. The goal of the present paper is to demonstrate how these previous results can be used in conjunction with data on wood burning activity, appliance ownership, and wood species availability to construct regional average residential wood smoke source profiles for use in chemical mass balance calculations. The regional variability of wood smoke organic chemical composition will be illustrated by particular reference to differences in emission factors of ten of the most important organic compounds in wood smoke.

7.2 Methods

The method for calculating composite regional source profiles for residential wood combustion is somewhat analogous to the process of creating weighted overall emissions profiles for motor vehicles based on the mix of vehicle types in the fleet and selected source emissions data (13). In the case of residential wood combustion, data on the geographical distributions of appliance types and total wood use are combined with source testing results and data on the availability of individual wood species to calculate an overall emission profile for all residential wood combustion in a particular region.

The year 1995 was selected as the base year for this study. That year was chosen to correspond with a set of ambient samples collected for future comparison against the source test data using chemical mass balance receptor modeling techniques. First, the

amount of wood burned in each of the 48 contiguous United States and the District of Columbia was taken from U. S. Department of Energy (USDOE) data on energy sources for residential home heating (24). Values given in British thermal units (Btu) were converted to mass of wood burned using their stated conversion factors of 20 million Btu (20.1 GJ) per cord and 1.25 short tons (1134 kg) per cord of wood. Additional data from the USDOE on the amount of wood burned as the main space-heating fuel in each U.S. census division in 1993 was used to apportion wood consumption between primary and secondary home heating purposes (25). The difference between total wood consumption and primary heating wood consumption is defined as secondary wood consumption within each U.S. census division. The resulting primary vs. secondary fractions in each U.S. census division were applied to each state's total wood consumption estimates.

Next, both primary and secondary wood consumption in each state was divided into wood burned in wood stoves and wood burned in fireplaces. This was accomplished using USDOE data on heating equipment used by households that use wood as a primary heating fuel and households using wood as a secondary heat source (26, 27). All wood burning appliances other than heating stoves were assumed to be fireplaces, although this figure may include a small number of wood burning furnaces. In order to best approximate the target year of 1995 and to lessen statistical errors associated with small sampling numbers in the surveys, 1993 and 1997 data from USDOE were averaged. The fraction of wood use by wood stoves and fireplaces within each U.S. census region and for both primary and secondary wood consumption were applied to the corresponding state totals for primary and secondary wood burning. The total amount of wood burned

in each state, apportioned between fireplaces and wood stoves, was calculated as the sum of primary and secondary consumption by each of the two wood burning appliance types.

Existing tree stand inventory data from the U. S. Forest Service show the wood species that are most abundant in each state (28). Making the assumption that people burn the wood species which grow in their vicinity (29), the wood burned in each state is apportioned between tree species in direct proportion to the standing tree species distribution within that state. Tree species data from Oregon and the District of Columbia were not available so the data for Washington State and Maryland were applied, respectively.

The wood use data described above next were translated into emissions estimates for wood combustion in fireplaces and wood stoves in each state. Emission factors per kg wood burned for components such as fine particle mass, organic carbon, and over 200 individual organic compounds have been previously determined for the fireplace and wood stove combustion of the most available wood species in the United States (2, 4-7). The fine particle emissions from the fireplace combustion of 22 wood species, chosen for their high level of national availability based on the same forestry surveys mentioned above, were examined in a set of comprehensive source tests. The top five nationally available wood species were also tested in a wood stove operated without emissions controls. A complete list of the tested wood species, along with the method for calculating their levels of availability, is provided in a previous work (2). While it is impractical to conduct source tests on every wood species burned in the United States, the wood species chosen for testing in the fireplace experiments conducted here account for approximately 60% of the wood burned nationally. For the remaining wood species

for which source tests were not performed, emission factors were estimated based on the results for the other woods. The composition of the emissions from all examples of oak, maple and pine woods tested were averaged within their respective groups and then used to represent all other untested oak, maple and pine species. For all remaining woods, the overall average emission characteristics for hardwoods and softwoods were utilized. Wood stove emission factors for the one oak and one pine species tested were applied to all oak and pine species burned in wood stoves, respectively. Average wood stove emission factors derived from the two maple species tested were applied to all other maple species burned in wood stoves. All other woods burned in wood stoves were represented using the average hardwood or softwood emission factors for wood stove combustion as appropriate. Overall emissions factors for each chemical species of interest were calculated for each state by summing the emissions of that chemical species across all of the wood types burned in the state.

Several qualities are desired when seeking to define potential particle-phase organic tracers for specific emissions sources. A high molecular weight corresponding to a low vapor pressure is important to ensure that the compound partitions primarily into the particle phase. High emission levels increase the likelihood that the compound can be detected in ambient samples. Compounds that are unique to a particular source are especially sought after as such compounds facilitate the chemical mass balance calculations. Finally, useful tracer compounds should react slowly enough in the atmosphere to survive transport between source and receptor site. Using these criteria, ten organic compounds that act as potential markers for wood smoke from among the over 200 compounds inventoried were selected to demonstrate regional variations in

residential wood combustion source profiles. The names and structures of these compounds are shown in Figure 7.1. A discussion of their usefulness as wood smoke tracers is reserved for the Results and Discussion section.

Using the appropriate emission factors, the total 1995 residential wood combustion emissions of fine particle mass, organic carbon, and the ten selected tracer compounds were calculated for each of the 48 contiguous United States. The state totals were then combined into regions corresponding to the ten U. S. Environmental Protection Agency regions, excluding Alaska and Hawaii. Results for individual organic compounds are stated as a fraction of the total fine particle organic carbon emitted in wood smoke in each region.

7.3 Results and Discussion

Table 7.1 lists selected results of the calculations for fine particle emissions from residential wood combustion in the contiguous United States in 1995, organized by EPA region. Total $PM_{2.5}$ emissions are normalized by mass of wood burned, land area and population in order to compare the emission characteristics from region to region. Normalizing by mass of wood burned yields regional composite emission factors which include both fireplace and wood stove combustion. Emission factors ranged from 2.8 g/kg wood burned in the Pacific Northwest to 4.7 g/kg in EPA Region 7 encompassing Iowa, Kansas, Missouri, and Nebraska. The regions in the central U.S. tended to yield higher emission factors per unit wood burned than the regions located on the east or west coast. This trend is due to a greater prevalence of fireplaces which produce higher fine particle emissions than wood stoves.

Figure 7.1. Names and structures of the organic compounds selected as wood smoke tracers for this study

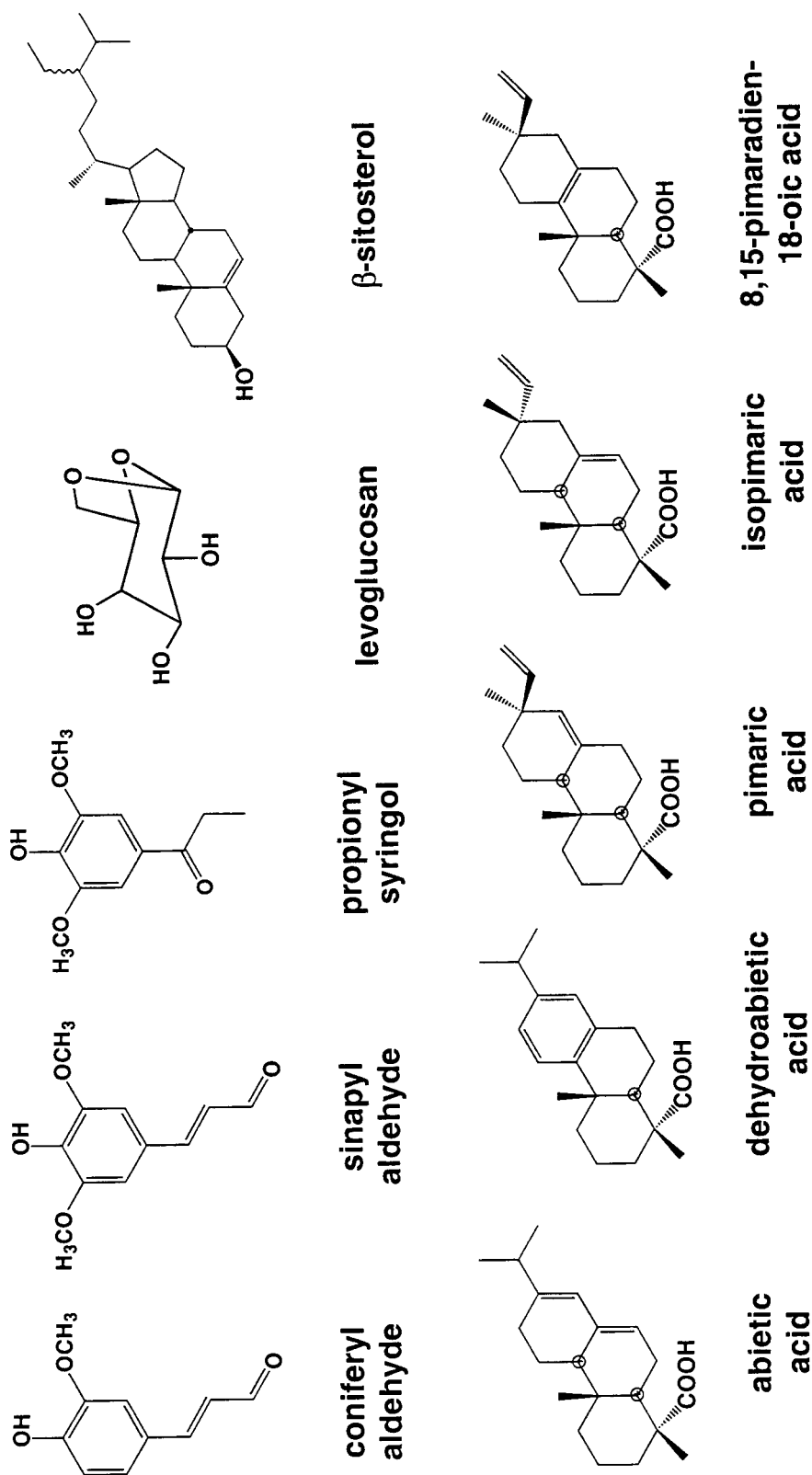


Table 7.1. Results by EPA Region for Residential Wood Combustion (RWC) Emissions in 1995

U.S. EPA Region	States Included	Total Wood Burned for RWC (10 ³ metric tons)	PM _{2.5} Emissions from RWC (10 ³ metric tons)	PM _{2.5} Emission Factor for RWC (g/kg wood burned)	PM _{2.5} Emissions per land area (kg/km ²)	PM _{2.5} Emissions per capita (kg/individual)	PM _{2.5} Organic Carbon (10 ³ metric tons)	Levoglucosan Emissions (10 ³ metric tons)
1	CT, ME, MA, NH, RI, VT	2,900	10	3.7	65	0.79	7.6	1.0
2	NJ, NY	4,300	15	3.4	100	0.57	11	1.5
3	DE, MD, PA, VA, WV, DC	3,800	15	3.9	47	0.55	11	1.5
4	AL, FL, GA, KY, MS, NC, SC, TN	6,400	25	3.9	26	0.51	18	2.3
5	IL, IN, MI, MN, OH, WI	4,900	22	4.4	26	0.45	17	2.4
6	AR, LA, NM, OK, TX	2,300	9.8	4.2	6.9	0.32	7.7	0.88
7	IA, KS, MO, NE	1,700	8.3	4.7	11	0.67	6.2	0.93
8	CO, MT, ND, SD, UT, WY	1,000	4.1	3.9	2.7	0.48	3.1	0.47
9	AZ, NV, CA	4,400	15	3.5	16	0.41	12	1.8
10	ID, WA, OR	1,900	5.3	2.8	8.4	0.55	4.4	0.85

On a per unit land area basis, Table 7.1 shows that fine particle emissions from residential wood combustion are most concentrated in the Northeast where population density is generally higher and cooler weather increases the need for home heating. In Western states that have lower population densities and/or warmer climates, the emissions density per unit land area is considerably less. On a per capita basis, fine particle residential wood combustion emissions are highest in New England and trend lower towards the west. The notable exception is EPA Region 7, which is explained by high emission factors from the types of wood burned in those states as well as the aforementioned prevalence of fireplaces. Table 7.1 also shows that the majority of fine particulate mass emitted from residential wood combustion consists of organic carbon, a result that is consistent with previous work (1, 2, 4-7). A detailed listing of the organic species which make up the organic carbon mass are given in these previous papers along with mass balances showing the major classes of organic compounds emitted as a fraction of total organic compound mass.

The cellulose pyrolysis product, levoglucosan, has been proposed previously as a general organic tracer for wood smoke particles (30, 31), and has been used successfully in chemical mass balance calculations to aid in apportioning ambient fine particle mass to wood combustion (14). This compound is non-volatile, existing predominantly in the particle phase as shown by source tests on fireplace combustion conducted by Schauer et al., (1). The presence of levoglucosan in the atmosphere, as well as its atmospheric stability with respect to acid-catalyzed hydrolysis in aqueous droplets, has been demonstrated (31). The very high emission factors for levoglucosan are shown in Table 7.1, with between 9 and 16% of the total fine particle mass emitted from residential wood

combustion consisting of this single compound. The presence of levoglucosan in ambient samples, its apparent atmospheric stability, and its high emission factor make it an ideal marker for wood smoke in general. Figure 7.2 displays regional levoglucosan emissions in a manner useful as input to chemical mass balance receptor modeling calculations; levoglucosan emissions are normalized to total particulate organic carbon mass. It is evident that a single levoglucosan emission factor might not be applicable to residential wood combustion throughout the United States. Woods burned in the Pacific Northwest emit greater relative quantities of levoglucosan than the other regions, while considerably lower relative amounts are emitted in the region that includes Texas. If one is to use levoglucosan as a wood smoke tracer, regional differences in wood and appliance types should be considered when developing a source profile for chemical mass balance modeling purposes.

Regional variations like those observed for levoglucosan emissions from residential wood combustion are also seen in the emissions of other potential organic wood smoke tracers. Two lignin pyrolysis products, coniferyl aldehyde and sinapyl aldehyde, are known components of wood smoke (2, 4-7) which also exist primarily in the particle phase of wood smoke emissions (14). The substituted guaiacol compound, coniferyl aldehyde, is found in the smoke from the combustion of both hardwoods and softwoods. Sinapyl aldehyde, a substituted syringol compound, is only found in the emissions from hardwood combustion. Regional differences in hardwood/softwood availability thus translate into regional differences in the emissions profiles of these compounds, as shown in Figure 7.3. In the Western U. S. where hardwoods are less available than in other regions east of the Rocky Mountains, emissions of sinapyl

Figure 7.2. Levoglucosan emissions from residential wood combustion in mg/g organic carbon

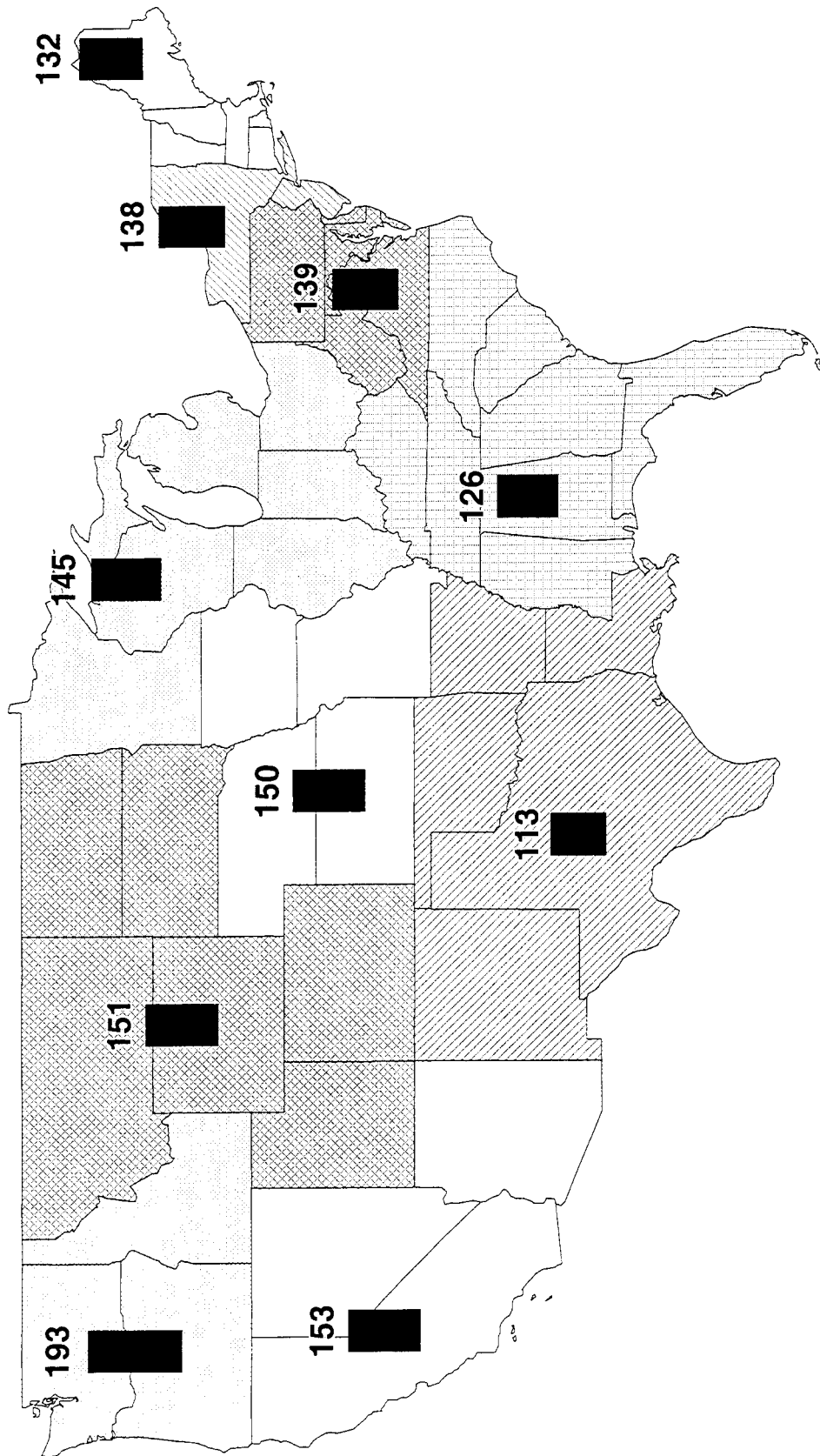
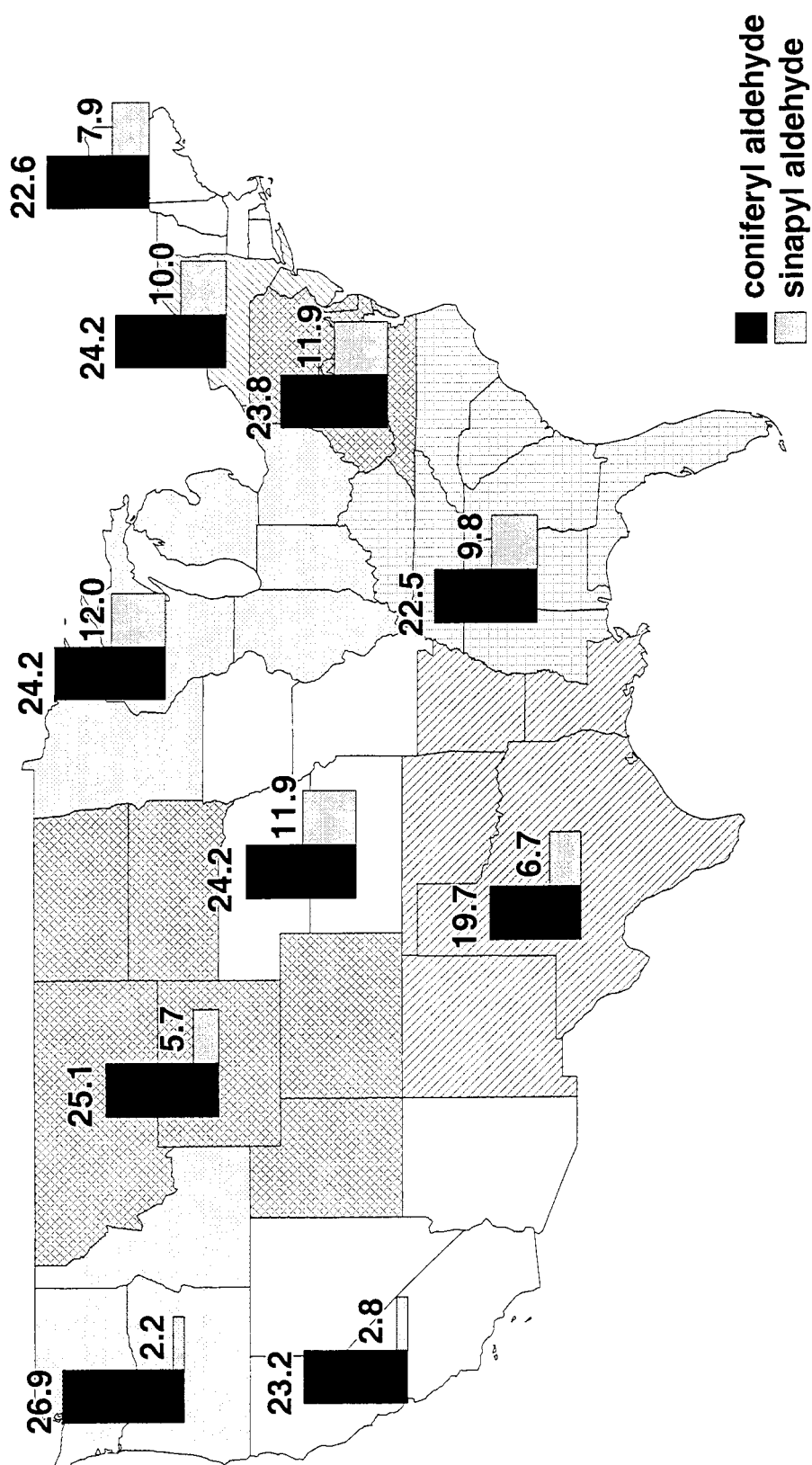


Figure 7.3. Coniferyl aldehyde and sinapyl aldehyde emissions from residential wood combustion in mg/g organic carbon

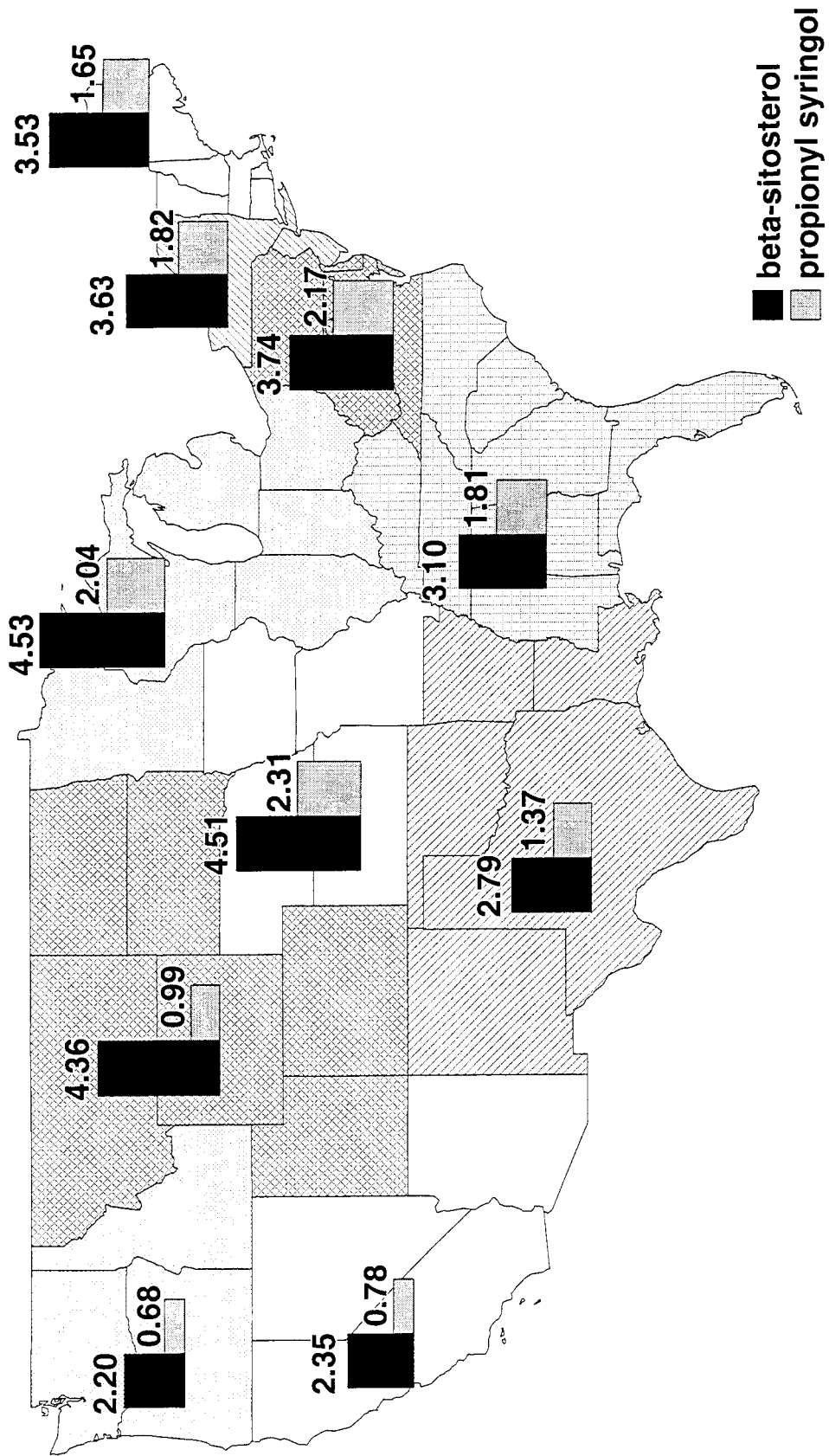


aldehyde as a fraction of fine particle organic carbon are relatively low, while coniferyl aldehyde is emitted at similar levels relative to fine particle organic carbon within all of the regions. These two compounds have also been measured at relatively high concentrations in ambient samples from the San Joaquin Valley of California (14). The chemical mass balance model accompanying that study was able to distinguish between hardwood and softwood smoke in the atmosphere by using substituted syringols as tracers for hardwood smoke.

Another potential wood smoke marker emitted primarily from hardwood combustion is the lignin pyrolysis product, propionyl syringol. This substituted syringol compound was measured in ambient samples and used successfully as a hardwood combustion marker in the San Joaquin Valley study (14). It is a known component of wood smoke (2, 4-7) which has been shown to exist primarily in the particle phase (1). There are no data available concerning its atmospheric stability. Figure 7.4 shows the regional variation in the emissions of this compound which is driven by the same hardwood and softwood availability patterns observed above for sinapyl aldehyde.

Also shown in Figure 7.4 are the regional emission factors for β -sitosterol, another potential wood smoke marker. β -Sitosterol is a phytosteroid present in plant lipids (32) which volatilizes during incomplete combustion and subsequently re-condenses into the particle phase. Its high molecular weight assures its complete partitioning into the particle phase. β -Sitosterol has been measured in ambient particle samples (30) but has not yet been used in chemical mass balance calculations. The emission factors of β -sitosterol can vary widely depending on the wood species being burned (2, 4-7). However, using our source test data combined with wood use data, it is

Figure 7.4. Beta-sitosterol and propionyl syringol emissions from residential wood combustion in mg/g organic carbon

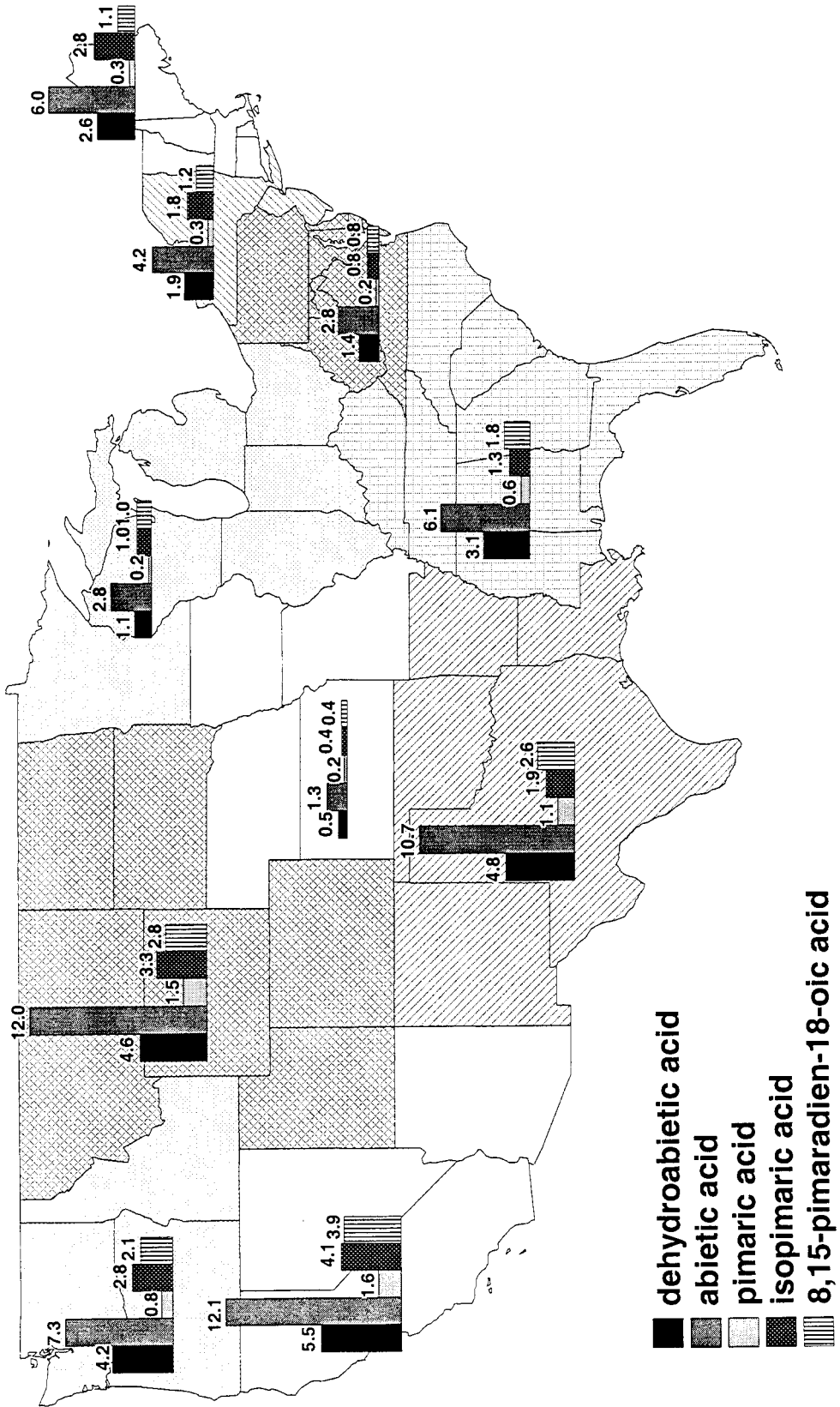


possible to arrive at regionally averaged emission factor estimates for this compound. Generally, more β -sitosterol is emitted from hardwood combustion than from softwood combustion. The lower β -sitosterol emission factor in the Western U. S. seen in Figure 7.4 are likely due to the lesser availability of hardwoods in the West, as mentioned before.

The final class of organic wood smoke markers examined in this study consist of resin acids. These resin acids are derived from conifer wood resins or their thermal alteration products (23). Therefore, they are emitted almost exclusively from softwood combustion as has been demonstrated previously (2, 4-7). Resin acids have been found only in the particle phase of wood smoke emissions (1). Figure 7.5 shows the regional variation in the relative emission factors of these five resin acids. Pimaric acid, isopimaric acid and 8,15-pimaradien-18-oic acid have all been measured in ambient samples and have been used previously in chemical mass balance calculations (14). Abietic acid and dehydroabietic acid have been included in Figure 7.5 due to their generally higher emission factors. The higher level of softwood combustion in the western states leads to significantly higher emissions of resin acids in the West when compared to the Eastern U. S. Region 7 (IA, KS, MO, NE) shows very low resin acid emissions presumably due to the low availability of softwoods in that area.

Figure 7.5 shows that the relative amounts of individual resin acids emitted from residential wood combustion can vary regionally. For instance more isopimaric acid is emitted than 8,15-pimaradien-18-oic acid in the Western and Northeastern regions. This trend is reversed in the other regions of the U. S and is a result of different emission factors of resin acids from the different softwood species available in these regions.

Figure 7.5. Resin acid emissions from residential wood combustion in mg/g organic carbon



When used together with the substituted syringol markers discussed above, the inclusion of resin acids in chemical mass balance models can aid in distinguishing between hardwood and softwood smoke. Since differences among the emission characteristics from different softwood species can lead to different emission profiles in different regions, it is important that receptor modeling calculations for wood smoke be based on the wood species and appliance type distributions that exist upwind of the particular receptor site of interest.

7.4 Conclusions

Chemical mass balance receptor models that use organic compounds as tracers for specific emissions source types are an important tool in determining the source contributions to ambient fine particle samples. The success of models of this type relies on having accurate source chemical composition profiles as input. Residential wood combustion is one of the largest sources of fine particle emissions to the atmosphere in North America. Since wood burning practices and activities can vary geographically, residential wood combustion chemical composition profiles also differ by region. The approach outlined in this paper, when combined with detailed emissions data from source testing, provides a method for calculating regionally averaged residential wood combustion source signatures. Comparison of regionally averaged compound-specific emissions factors shows that the relative amount of the general wood smoke tracer levoglucosan emitted per gram organic carbon in wood smoke varies by less than a factor of two across all regions of the United States. Within that factor of two, a quick estimate of wood smoke particle concentrations in the U. S. atmosphere can be obtained in

situations where one is fairly sure that residential wood combustion is the source of the wood smoke. Other compounds that are directly linked to hardwood combustion vary over a wider range which reflects regional differences in the prevalence of hardwoods vs. softwoods. The emission factor for sinapyl aldehyde, which is derived largely from hardwoods, varies by more than a factor of five between the geographic regions studied. By quantifying the similarities and differences between the wood smokes generated in different regions, source chemical composition profiles can be developed that will help to quantify the amount of wood smoke in the atmosphere and that might even act as a signature for the geographic origin of a particular air mass.

7.5 Acknowledgments

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7.6 References

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Chapter 8

The Contribution of Biomass Combustion to Ambient Fine Particle Carbon Concentrations Throughout the United States

8.1 Introduction

According to the United States Environmental Protection Agency inventory estimates, biomass combustion is a significant source of atmospheric fine particle pollution in the United States. For the calendar year 1995, 19% of all primary fine particle emissions came from biomass combustion sources (1). The most important biomass combustion sources were residential wood combustion (7%), prescribed burning (6%), residential open burning (3%), wildfires (2%), and agricultural burning (1%). Inventory estimates such as these can be used in combination with atmospheric transport models to predict fine particle concentrations at specific ambient sampling locations (2, 3). However, these source-oriented models rely heavily on inventory estimates which are often based on rough approximations of human activity and emission factors. For area sources such as biomass combustion, it is especially difficult to make accurate inventory estimates due to a lack of reliable record keeping and highly variable emission factors (4-8).

Receptor-oriented models, which calculate the best combination of source contributions needed to reconstruct the chemical composition of an ambient sample (9), provide an alternative to source-oriented transport models. Chemical mass balance receptor models do not depend on complex atmospheric transport calculations or accurate source activity data, but they do require accurate chemical characterization of the different source types. Many previous chemical mass balance studies have used the

elemental composition of particulate matter emitted from sources to identify the relative source contributions to ambient samples (10-14). But often, the elemental composition of source emissions are not sufficiently unique to distinguish between source types. By using a subset of the hundreds of individual organic compounds previously identified in source and ambient aerosol samples (4-8, 15-20), apportionment of a greater number of source types is possible (21, 22).

The present paper employs a chemical mass balance receptor model to determine the source contributions to ambient fine particle samples collected throughout the United States. Filter samples from mostly rural sampling locations collected as part of the IMPROVE and NESCAUM monitoring networks were combined into semi-annual composites and analyzed for specific organic tracers. While the primary focus of this study is to determine the importance of biomass combustion nationally, three other source types thought to be important in rural areas were also included in the model. Speciated organic compound source profiles for all source types were taken from previous source testing studies on residential wood combustion, motor vehicles, soil/road dust, and vegetative detritus. While these source profiles may not be ideal for all locations in the United States, the model results are a good first approximation for the geographically widest chemical mass balance model calculation attempted to date.

8.2 Methods

8.2.1 Ambient Samples

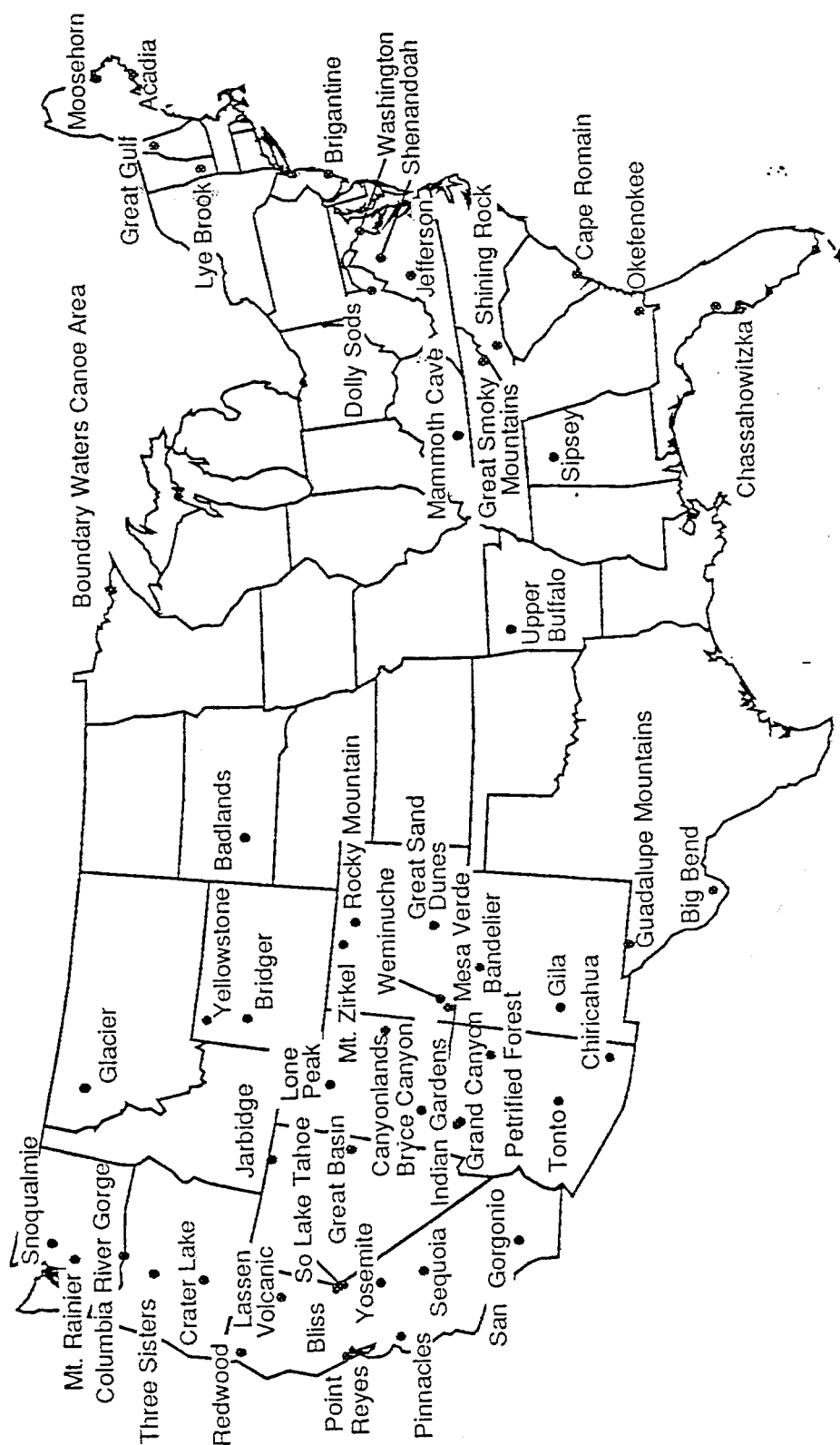
The majority of the ambient filter samples considered in this study were collected as part of the IMPROVE (Interagency Monitoring of PROtected Visual Environments)

Network, a long term air sampling program designed to protect visibility in national parks and wilderness areas (23). The sampling sites for this program are generally located within national parks, national forests, wilderness areas, wildlife refuges and national monuments throughout the United States with two additional sites in British Columbia, Canada. This sampling network represents the most extensive fine particle sampling campaign in the United States in which filters conducive to organic compound speciation are collected. A map of the IMPROVE network sites at which quartz fiber filters were collected for carbon analysis is given in Figure 8.1. At each of these sites, 24-hour fine particle samples ($<2.5\ \mu\text{m}$) were collected twice a week, Wednesday and Saturday, on 35 mm quartz fiber filters. Subsequent to shipping and analysis, the remaining filters were stored in a cryo-freezer at the Desert Research Institute (DRI) in Reno, Nevada.

Archived IMPROVE network quartz fiber filter samples from the calendar year 1995 were retrieved from the DRI storage freezer for subsequent organic speciation analysis. In order to maintain an archived filter set at DRI, filters were cut and only one-half of each filter was obtained. Having been previously analyzed for elemental and organic carbon by the DRI thermal optical reflectance (TOR) method (24), most of the retrieved filters were missing one or more $0.52\ \text{cm}^2$ circular punches taken for the TOR method. The missing holes were split evenly between filter halves such that one-half of the remaining active filter area was used in the analysis.

Over 7000 filters were cut, collected and then grouped into semi-annual composite samples: a warm season composite (April – October) when forest fires are expected to be active; and a cold season composite (January-April, November, December) during which residential wood combustion is more prevalent. This division

Figure 8.1. IMPROVE Program sampling site locations

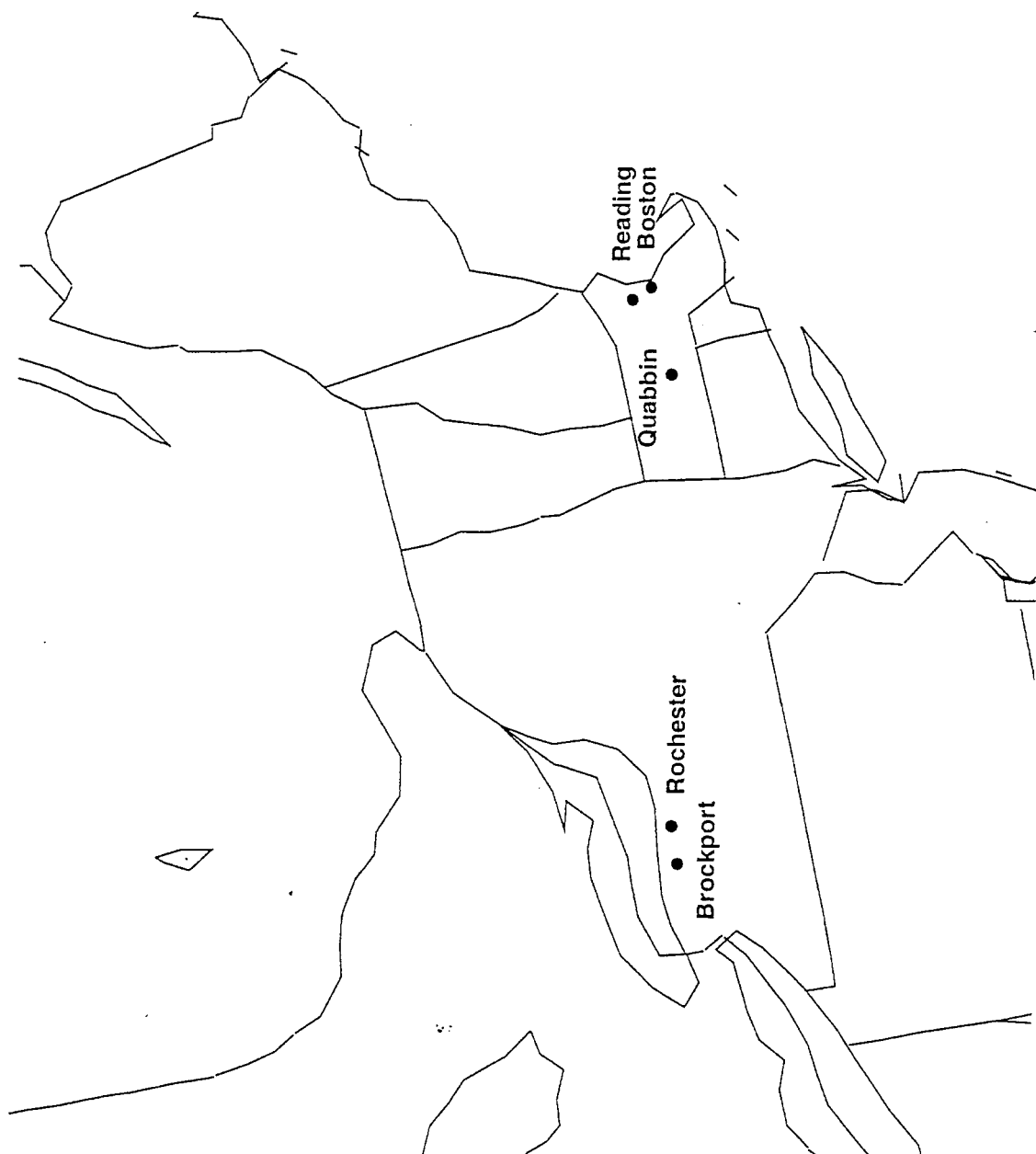


results in an equal number of sampling days in each of the two composites. Several individual filters, collected on days when historical fire records indicated a nearby wildfire and chemical analysis confirmed very high organic carbon and potassium levels (potassium has been used previously as a marker for biomass combustion (25)), were not included in the composite samples and were analyzed separately.

Due to the large scale of the IMPROVE sampling program, it is inevitable that some of the filters for scheduled sampling days are missing. Thus, the composite samples do not always represent a perfect six-month average. However, since less than 5% of the sampling events were missing and these missing days tended to be randomly distributed, the composites still represent a good sampling of the ambient fine particulate material at each site over the six month period. Furthermore, the varying number of filter punches taken for repeat TOR analysis results in a slightly unequal contribution of the active filter area from different sampling days. However, a comparison of ambient fine particle mass concentrations with the fine particle mass in the composite sample based on filter area showed that the associated error is less than 5% in all cases.

The filters from five additional sites in the Northeastern U. S. from the NESCAUM sampling program were included in our analysis. Figure 8.2 shows the location of the sampling sites. The NESCAUM samples were collected on 47 mm quartz fiber filters for 24 hours, every sixth day for the entire year of 1995. The entire filter from each sampling day, minus one or two punches taken for carbon analysis, was included in the appropriate semi-annual composite using the same month-based divisions described above.

Figure 8.2. NESCAUM Program sampling site locations



8.2.2 Chemical Analysis

Selected chemical analyses had been performed previously by DRI as part of their routine sample analysis for the IMPROVE project. Thus, the Al and Si data used in this study were provided by the X-ray Fluorescence (XRF) analysis of DRI. In addition, the Total Carbon (TC) data for the IMPROVE filters was provided by the TOR organic analysis conducted at DRI. The Si and Al data for the NESCAUM filters were also analyzed by DRI using XRF. However, the carbon analysis for these filters was conducted using the thermal optical transmission method (TOT) developed by Birch and Cary (26).

The individual organic compounds present in the ambient composite fine particle samples were determined using methods established by Mazurek et al. (27) and Rogge et al. (16). Briefly, the collection of quartz fiber filters in each composite sample are spiked with a mix of deuterated internal recovery standards and then extracted by mild sonication twice in hexane (Fischer Optima Grade) and three times in a benzene/isopropanol mixture (2:1) (benzene: E&M Scientific; isopropanol: Burdick & Jackson). Extracts are filtered, combined, and reduced in volume to approximately 1 ml. The large number of previously cut filters in each of the composite samples led to a high level of filter fragments that could not be filtered out of the extract. By repetitive solvent rinses and decanting procedures, the majority of the filter debris was removed with very little sample losses. The 1 ml extract is then split and one of the fractions is derivatized with diazomethane to convert organic acids to their methyl ester analogs which are more amenable to GC/MS analysis. The derivatized and underivatized sample fractions are analyzed by GC/MS on a Hewlett-Packard GC/MSD (GC model 5890, MSD model

5973) using a 30 m x 0.25 mm diameter HP-5MS capillary column (Hewlett-Packard) using an auto-injector. Hundreds of authentic standard mixtures have been prepared for the positive identification and quantification of many of the organic compounds found in ambient particulate matter. These standard suites also contain the same set of internal deuterated standards that were added to our samples. Relative response factors for each compound in the standard mixtures can be calculated relative to an appropriate deuterated compound. These response factors can then be used to quantify each compound in our samples relative to the same internal deuterated compound. When quantitative standards are not available for a given compound or compound class, significant effort is made to obtain a non-quantitative secondary standard that can be used for unique identification of the organic compounds. When a secondary standard is not available, interpretation of mass spectra and mass spectral libraries is used to aid in identification. Quantification of compounds for which primary standards are not available has been estimated from the response factors for compounds having similar retention times, chemical structures, and degrees of fragmentation.

8.2.3 Source Apportionment

The source apportionment calculations were conducted using EPA-CMB8.2, the latest version of the chemical mass balance software developed by the USEPA. This receptor model uses the chemical properties of particles as measured at source and receptor site to quantify the source contributions to receptor concentrations. It consists of a solution to a set of linear equations that express each receptor chemical concentration as

a linear sum of products of source profile abundances and source contributions. The set of linear equations can be expressed by

$$c_{ik} = \sum_{j=1}^m a_{ij} s_{jk}$$

where c_{ik} is the concentration of chemical species i in the fine particles at receptor site k , m is the total number of source types, a_{ij} is the relative concentration of chemical i from source j , and s_{jk} is the contribution to total fine particle mass at site k originating from source j .

Rather than apportioning total fine particle mass, this study only tries to determine the source contributions to total ambient fine particle carbon at each receptor site. Previous studies have used organic carbon as the bulk quantity to be apportioned (21, 22). However, organic carbon could not be used in the present analysis due to differences in carbon analysis methods. It has been shown that the elemental carbon (EC) and organic carbon (OC) splits in the TOR and TOT carbon analysis methods are not the same (28) due to different temperature programs. The TOR method tends to measure significantly higher elemental carbon levels than the TOT method. However, the total carbon measurement is relatively consistent between the two methods. In this study, most of the ambient samples were analyzed by TOR while all of samples used to generate our source profiles were measured using TOT. Thus, in order to have a comparable measurement between source and receptor, and also due to the large variation in the suggested EC correction, total carbon was chosen as the quantity to apportion. In either case, whether organic or total carbon is the apportioned quantity, the model results yield information

that is very similar to results when apportioning total fine particle mass because most of the non-carbon components of ambient particles are secondary inorganics.

8.2.4 Source Profiles

Due to the mostly rural locations of the sampling sites, an effort was made to limit the number of sources in the mass balance calculation to those thought to be important in non-urban areas. While some of the following source profiles may not be ideal when applied to all regions of the U.S., they were selected because the analytical methods used to create the profiles are very similar to the methods used to analyze the ambient samples in this study.

The fine particle emissions from biomass combustion are the main focus of this study. Source profiles for biomass combustion were based on an extensive series of source tests conducted on wood burning in fireplaces and wood stoves (4-8). Regional wood smoke profiles, corresponding to the ten USEPA regions, were calculated in a manner similar to that described in a previous work (29). Briefly, U.S. census data on wood burning appliance use and ownership was combined with national forestry surveys to estimate the amount of each wood type burned in each state. Then, emission factors from the source tests are applied to this burning activity to arrive at regional source profiles for wood smoke. Due to the current lack of reliable organic compound source signatures on other biomass burning sources, such as wildfires and prescribed burning, the rough assumption was made that source profiles based on residential wood combustion are also representative of all biomass combustion sources.

The second fine particle source included in the model calculations are vehicular emissions. As mentioned above, the differences in carbon analysis methods precluded using elemental carbon as a distinct chemical species in the model. While fine particle elemental carbon emissions from diesel engines and gasoline engines differ significantly, the organic compound signature from these two sources are very similar and thus, not sufficiently linearly independent to use in the model calculations. Without elemental carbon as a fitting species, the contributions from diesel vehicle and gasoline vehicle sources are difficult to resolve. Therefore, a combined diesel and gasoline vehicle emission profile was taken from a tunnel study conducted in Los Angeles in 1993 by Fraser et al. (30). Due to differences in vehicle fleet mixes and fuel chemistries in different parts of the U.S., this source profile may not ideally represent vehicular emissions for the whole country. However, since detailed vehicular source signatures from every area are not available, the Los Angeles tunnel study results serve as a good first approximation.

The third fine particle source thought to be important in rural areas is road and soil dust. The chemical profile for this source is taken from a road and soil dust analysis conducted previously in the San Joaquin Valley of Central California (31). As was the case for the vehicular emissions, this profile may not be ideally representative of soil and road dust in all parts of the U.S. But since the analysis methods are similar to those used here, it was selected to represent soil and road dust throughout the country. The final source included in the model are vegetative detritus emissions generated as abrasion products from leaf surfaces. The source profile for vegetative detritus was taken from another Southern California study which used similar analysis techniques (17).

The numerous organic compounds quantified in the ambient fine particle samples provide a large set of chemical species for potential use in the chemical mass balance calculation. Tables 8.1a and 8.1b list the chemical species used in the model and the emissions profiles from each of the four source types. The cellulose pyrolysis product, levoglucosan, has been shown to be an excellent unique marker for biomass combustion in general (22, 32). Three of the most prevalent hopanes were used to track vehicular emissions (22). Fine particle silicon and aluminum were included primarily to help resolve the contributions from soil and road dust (22). Finally, n-alkanes between carbon number 27 and 33 were included as fitting species in the model. Many of the n-alkane emissions in this range come from vegetative detritus and exhibit the natural odd carbon number preference (17).

8.3 Results and Discussion

The source apportionment results from the chemical mass balance model were generally reasonable for almost all of the sampling locations. Table 8.2 gives the contribution of each of the four sources towards the total ambient carbon concentration at each site. The “other” contribution, the residual difference between the total carbon concentration and the calculated source contributions to total carbon, consists of carbon from other sources not included in the model and/or carbon from secondary organic particulate matter. While biomass combustion, dust, and vehicles contributed significantly to the carbon concentrations to varying degrees at each sampling location, vegetative detritus was not a major source of fine particulate carbon nationally. A sample of the results of the calculation is given in Figure 8.3 for the cold month composite in

Table 8.1a. Biomass Combustion Source Profiles for Input into EPA-CMB 8.2 Model. All values in milligram chemical species per gram total carbon.

Biomass Combustion by EPA Region										
Chemical Species	Region 1	Region 2	Region 3	Region 4	Region 5	Region 6	Region 7	Region 8	Region 9	Region 10
Heptacosane	0.01 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.03 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.04 ± 0.01	0.01 ± 0.01	0.02 ± 0.01
Octacosane	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.01	0.01 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.01 ± 0.01	0.00 ± 0.01	0.00 ± 0.01
Nonacosane	0.00 ± 0.01	0.00 ± 0.01	0.01 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01
Triacontane	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01
Hentriacontane	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01
Dotriacontane	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01
Tritriacontane	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01
Levoglucosan	115 ± 23	123 ± 25	128 ± 26	113 ± 23	135 ± 27	101 ± 20	143 ± 29	136 ± 27	134 ± 27	173 ± 35
Silicon	0.83 ± 0.25	0.68 ± 0.20	0.45 ± 0.13	0.61 ± 0.18	0.40 ± 0.12	0.64 ± 0.19	0.26 ± 0.08	0.68 ± 0.20	0.92 ± 0.28	0.88 ± 0.26
Aluminum	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.10
17a(H),21b(H)-hopane	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01
17a(H),21b(H)-29-norhopane	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01
22,29,30-trisnorhopane	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01

Table 8.1b. Additional Source Profiles for Input into EPA-CMB 8.2 Model. All values in milligram chemical species per gram total carbon.

Chemical Species	Vegetative Detritus	Soil/Road Dust	Motor Vehicles
	All Regions	All Regions	All Regions
Heptacosane	2.47 ± 0.49	0.22 ± 0.04	0.48 ± 0.10
Octacosane	0.70 ± 0.14	0.14 ± 0.03	0.36 ± 0.07
Nonacosane	18 ± 4	0.42 ± 0.08	0.59 ± 0.12
Triacontane	1.30 ± 0.26	0.12 ± 0.02	0.38 ± 0.08
Hentriacontane	28 ± 6	0.13 ± 0.03	0.43 ± 0.09
Dotriacontane	2.28 ± 0.46	0.05 ± 0.01	0.22 ± 0.04
Tritriacontane	13.9 ± 2.8	0.05 ± 0.01	0.15 ± 0.03
Levoglucosan	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01
Silicon	250 ± 55	734 ± 22	4.0 ± 2.0
Aluminum	77 ± 13	255 ± 15	6.0 ± 6.0
17a(H),21b(H)-hopane	0.00 ± 0.01	0.00 ± 0.01	0.38 ± 0.08
17a(H),21b(H)-29-norhopane	0.00 ± 0.01	0.00 ± 0.01	0.25 ± 0.05
22,29,30-trisnorhopane	0.00 ± 0.01	0.00 ± 0.01	0.13 ± 0.03

Table 8.2. Chemical Mass Balance Model Results. The data show the contribution of each source to total fine particle carbon concentrations at each sampling site in both the warm and cold month composite samples.

Sampling Location	Cold Month Composite					Warm Month Composite				
	Biomass Combustion	Vegetative Detritus	Soil/Road Dust	Motor Vehicles	Other ^a	Biomass Combustion	Vegetative Detritus	Soil/Road Dust	Motor Vehicles	Other ^a
Acadia NP, ME	17.9%	0.5%	4.7%	38.6%	38.3%	8.1%	0.4%	3.4%	24.4%	63.7%
Great Gulf Wilderness, NH	*	*	*	*	*	32.2%	1.2%	3.3%	13.0%	50.3%
Lye Brook Wilderness, VT	11.4%	0.3%	6.2%	49.4%	32.7%	6.9%	1.0%	4.8%	19.6%	67.7%
Moosehorn NWR, ME	23.1%	2.1%	3.1%	38.5%	33.2%	15.2%	2.3%	2.8%	16.4%	63.4%
Brigantine NWR, NJ	28.5%	0.6%	4.8%	23.7%	42.6%	4.2%	1.1%	5.3%	12.4%	76.9%
Dolly Sods Wilderness, WV	81.1%	0.5%	4.7%	24.6%	OB	*	*	*	*	*
Jefferson/James River Face, VA	71.6%	0.4%	18.4%	3.9%	5.7%	27.9%	0.7%	4.6%	9.2%	57.7%
Shenandoah NP, VA	26.3%	0.5%	7.5%	19.1%	46.5%	*	*	*	*	*
Washington, DC	25.0%	0.3%	3.5%	34.9%	36.3%	5.7%	0.8%	4.0%	15.4%	74.0%
Mammoth Cave NP, KY	25.4%	0.6%	6.0%	21.6%	46.4%	*	*	*	*	*
Okefenokee NWR, GA	21.8%	0.8%	3.6%	14.5%	59.2%	9.5%	1.2%	15.0%	9.7%	64.6%
Cape Romain NWR, SC	26.5%	0.8%	3.9%	12.8%	56.0%	6.2%	1.5%	13.2%	8.2%	70.9%
Shining Rock Wilderness, NC	14.1%	1.2%	10.8%	23.7%	50.2%	*	*	*	*	*
Sipsy Wilderness, AL	30.5%	3.4%	5.6%	11.7%	48.8%	11.9%	2.1%	7.1%	7.5%	71.3%
Boundary Waters Canoe Area, MN	13.5%	0.4%	8.6%	60.0%	17.4%	10.9%	1.5%	4.1%	27.4%	56.1%
Bandelier NP, NM	17.3%	0.7%	20.5%	32.9%	28.6%	8.4%	1.4%	22.5%	20.3%	47.4%
Big Bend NP, TX	4.4%	2.3%	50.9%	29.4%	13.0%	2.3%	2.0%	37.6%	20.3%	37.8%
Gila Wilderness, NM	41.7%	1.0%	12.7%	25.3%	19.3%	38.2%	3.3%	17.7%	12.7%	28.2%
Guadalupe Mountains NP, TX	12.5%	4.3%	36.8%	40.5%	5.9%	1.9%	3.5%	53.5%	18.6%	22.5%
Upper Buffalo Wilderness, AK	31.9%	1.4%	7.4%	12.3%	47.0%	11.3%	1.8%	14.4%	5.8%	66.9%
Badlands NP, SD	6.7%	0.9%	14.4%	30.8%	47.2%	6.9%	6.0%	12.3%	13.8%	61.0%
Bridger Wilderness, WY	7.5%	0.5%	19.3%	49.6%	23.1%	8.6%	1.9%	14.1%	28.1%	47.3%
Bryce Canyon NP, UT	1.7%	0.8%	24.9%	40.7%	32.0%	36.2%	2.0%	25.3%	21.7%	14.8%
Canyonlands NP, UT	3.3%	0.8%	26.2%	36.8%	32.9%	1.5%	4.0%	27.2%	25.1%	42.3%
Glacier NP, MT	64.1%	0.0%	3.5%	30.4%	2.0%	23.8%	0.6%	10.0%	15.3%	50.2%
Great Sand Dunes NM, CO	9.9%	0.7%	41.9%	21.3%	26.1%	3.9%	1.7%	41.9%	21.4%	31.0%
Lone Peak Wilderness, UT	16.2%	0.5%	14.3%	28.2%	40.7%	13.2%	2.2%	20.2%	30.8%	33.7%
Mesa Verde NP, CO	3.3%	0.3%	28.6%	63.6%	4.2%	1.8%	0.7%	30.8%	50.0%	16.8%
Mount Zirkel Wilderness, CO	4.3%	0.8%	21.6%	129.6%	OB	3.0%	1.7%	39.6%	45.9%	9.8%
Rocky Mountain NP, CO	10.5%	0.4%	26.5%	44.6%	18.0%	18.1%	1.0%	28.3%	17.5%	35.2%
Weminuche Wilderness, CO	7.9%	0.5%	29.1%	37.8%	24.7%	5.1%	0.9%	27.9%	24.5%	41.6%
Yellowstone NP, CA	37.1%	0.3%	13.0%	50.6%	OB	11.5%	1.4%	28.7%	22.2%	36.2%
Bliss State Park, CA	61.8%	1.2%	10.1%	37.9%	OB	15.5%	1.1%	15.4%	30.8%	37.2%
Chiricahua NM, AZ	3.2%	1.4%	32.7%	26.6%	36.1%	1.6%	1.4%	40.9%	21.4%	34.7%
Great Basin NP, NV	6.6%	0.4%	19.3%	23.4%	50.3%	3.3%	1.1%	28.0%	26.0%	41.5%
Grand Canyon NP, AZ	3.6%	0.4%	25.0%	32.4%	38.6%	1.9%	1.3%	27.0%	17.9%	51.9%
Indian Gardens, AZ	6.7%	1.3%	20.0%	31.5%	40.5%	3.3%	4.5%	29.6%	19.1%	43.5%
Jarbridge Wilderness, NV	10.2%	0.7%	19.5%	62.0%	7.7%	24.2%	1.7%	37.1%	23.4%	13.7%
Lassen Volcanic NP, CA	11.5%	1.2%	13.4%	32.9%	40.9%	11.4%	0.9%	18.4%	20.0%	49.3%
Petrified Forest NP, AZ	11.5%	0.3%	18.4%	33.2%	36.6%	4.3%	0.8%	30.4%	23.5%	40.9%

Sampling Location	Cold Month Composite					Warm Month Composite				
	Biomass Combustion	Vegetative Detritus	Soil/Road Dust	Motor Vehicles	Other*	Biomass Combustion	Vegetative Detritus	Soil/Road Dust	Motor Vehicles	Other*
Pinnacles NM, CA	32.8%	1.6%	3.8%	12.0%	49.9%	5.4%	2.6%	7.1%	11.9%	73.0%
Point Reyes National Seashore, CA	25.0%	0.6%	3.2%	28.1%	43.1%	8.0%	0.8%	4.5%	39.5%	47.1%
Redwood NP, CA	17.0%	0.3%	4.6%	29.5%	48.7%	34.0%	0.4%	3.3%	28.8%	33.5%
San Geronimo Wilderness, CA	*	*	*	*	*	2.0%	0.8%	18.0%	11.1%	68.1%
Sequoia NP, CA	131.3%	10.7%	0.3%	14.7%	OB	10.6%	1.0%	13.5%	13.9%	61.1%
South Lake Tahoe, CA	86.1%	0.4%	7.1%	22.3%	OB	43.1%	0.7%	15.0%	40.4%	0.8%
Tonto NM, AZ	11.0%	1.0%	16.7%	15.1%	56.2%	7.7%	2.8%	22.8%	12.6%	54.0%
Yosemite NP, CA	18.0%	0.6%	9.2%	38.4%	33.8%	9.2%	0.8%	9.7%	23.3%	57.0%
Abbotsford, BC, Canada	42.2%	0.7%	4.6%	33.2%	19.2%	19.8%	1.1%	8.2%	33.1%	37.7%
Chilliwack, BC, Canada	38.5%	0.5%	7.1%	28.0%	25.9%	20.7%	0.7%	6.1%	15.3%	57.2%
Columbia River Gorge, WA	29.0%	0.2%	3.2%	34.6%	32.9%	9.0%	0.5%	11.1%	29.7%	49.7%
Crater Lake NP, OR	6.0%	0.3%	9.8%	29.9%	54.0%	5.7%	1.0%	12.5%	21.8%	58.9%
Mount Ranier NP, WA	74.3%	0.0%	3.2%	42.2%	OB	26.2%	0.2%	3.6%	36.8%	33.2%
Snoqualmie National Forest, WA	21.4%	0.0%	6.5%	34.3%	38.0%	15.8%	0.4%	10.2%	32.3%	41.3%
Three Sisters Wilderness, OR	15.8%	0.2%	7.4%	45.4%	31.2%	13.2%	1.0%	7.7%	16.0%	62.1%
Kenmore Square, Boston, MA	11.8%	0.2%	2.9%	27.0%	58.1%	3.0%	0.2%	2.5%	25.2%	69.1%
Quabbin Reservoir, MA	30.4%	1.2%	5.3%	20.9%	42.3%	3.7%	1.2%	2.6%	7.6%	84.9%
Reading, MA	30.1%	0.4%	3.7%	23.5%	42.3%	7.4%	0.6%	3.7%	18.1%	70.2%
Brockport, NY	21.4%	3.0%	3.2%	18.2%	54.2%	17.3%	2.3%	4.4%	23.6%	52.4%
Rochester, NY	16.0%	2.2%	3.3%	38.3%	40.2%	5.9%	1.7%	3.9%	29.2%	59.3%

Abbreviations and Notes:

NP - National Park

NWR - National Wildlife Refuge

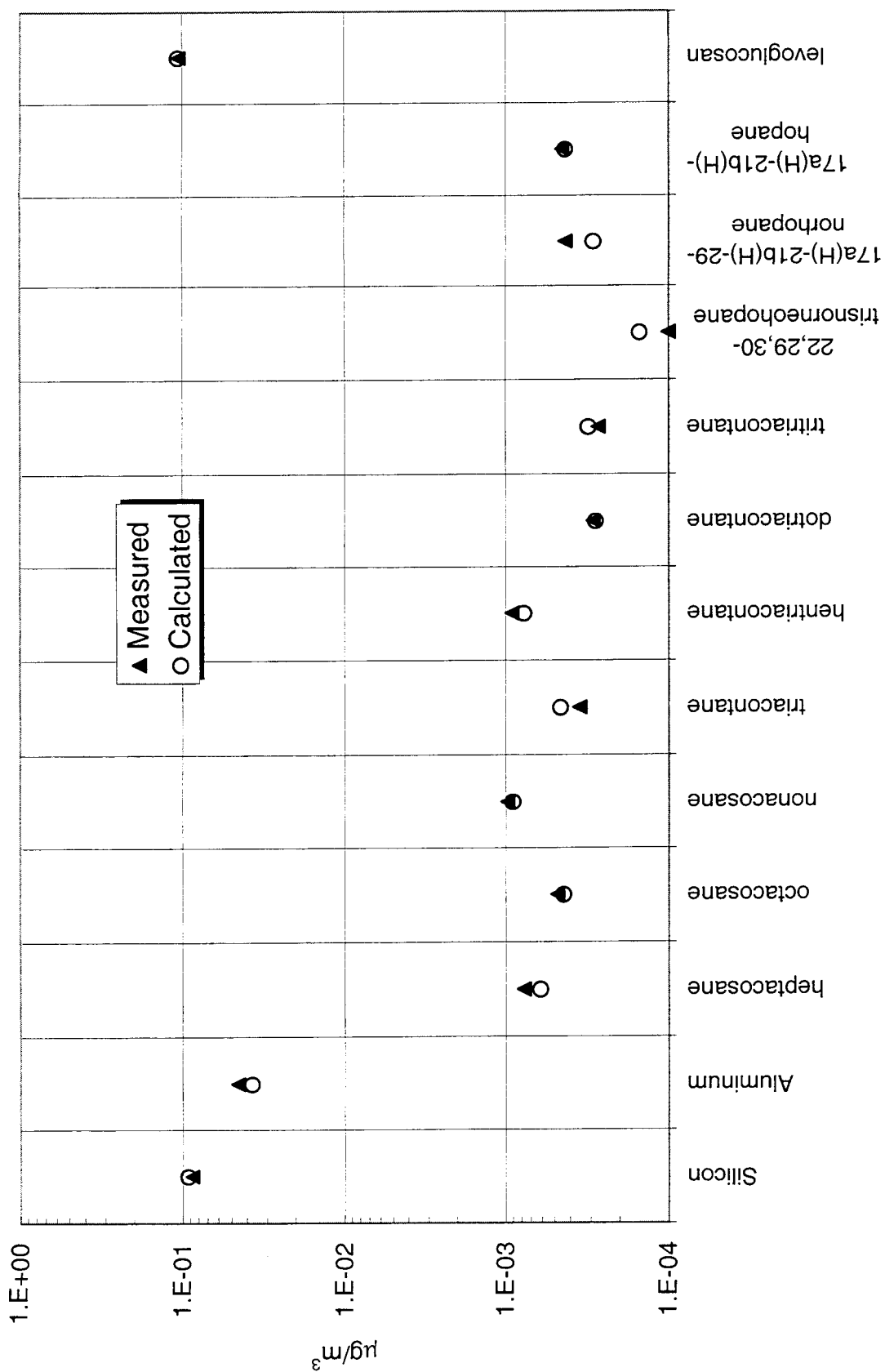
NM - National Monument

OB - Overbalance of total carbon

* Data missing due to missing sample, contaminated sample, or non-convergence of model

"Other" includes sources not included in the model and secondary organic particulate matter

Figure 8.3. Sample results for the Washington DC IMPROVE site in 1995, cold month composite, showing measured vs. calculated values for the chemical species used in the chemical mass balance model



Washington DC. There is excellent agreement between the calculated and measured values for each of the chemical species included in the model.

As mentioned above, four individual filters from days with wildfire events were kept apart from the composite samples and analyzed separately. The apportionment results from these episodes provide a check on the applicability of the residential wood combustion source profiles to actual forest fire emissions. Figure 8.4 shows that in each case, the model calculated that between 64 and 72% of the particulate carbon came from biomass combustion. The lack of significant contributions from motor vehicles on these days help confirm that these samples were primarily from a nearby forest fire event. Considering the wide range of combustion conditions within a forest fire and the suspected degree of variation in emission factors of organic compounds, the high biomass combustion contributions calculated for these samples show that the residential wood combustion profiles are roughly applicable to forest fires. Assuming that all the fine particulate carbon on these days was from the nearby fires, the slight under-prediction suggests that the relative levoglucosan emission factor from forest fires is approximately 30% less than that of residential wood combustion. The high contribution from vegetative detritus during the Yosemite and Sequoia fires may be a result of plant wax volatilization from foliage due to the heat of the fire rather than leaf abrasion products. The residential wood combustion source profiles do not include this phenomenon since foliar material is generally not burned in fireplaces or wood stoves.

Figure 8.5 shows the results of the apportionment at two selected sites, Washington DC and the Jefferson National Forest/James River Face Wilderness in Virginia. While the total fine particulate carbon at these two sites is similar for the warm

Figure 8.4. Model results for four individual filter samples collected on days with a nearby wildfire

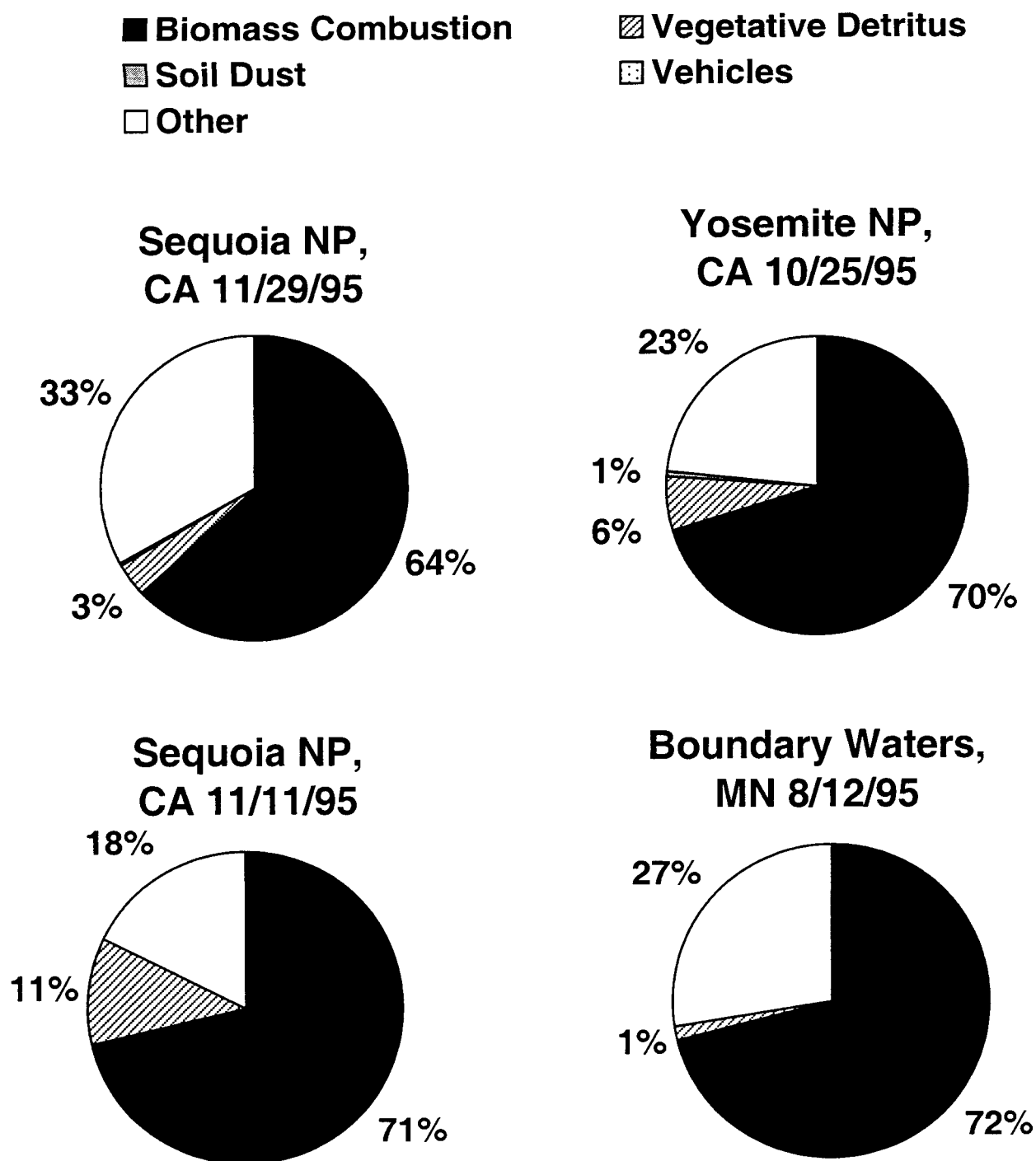
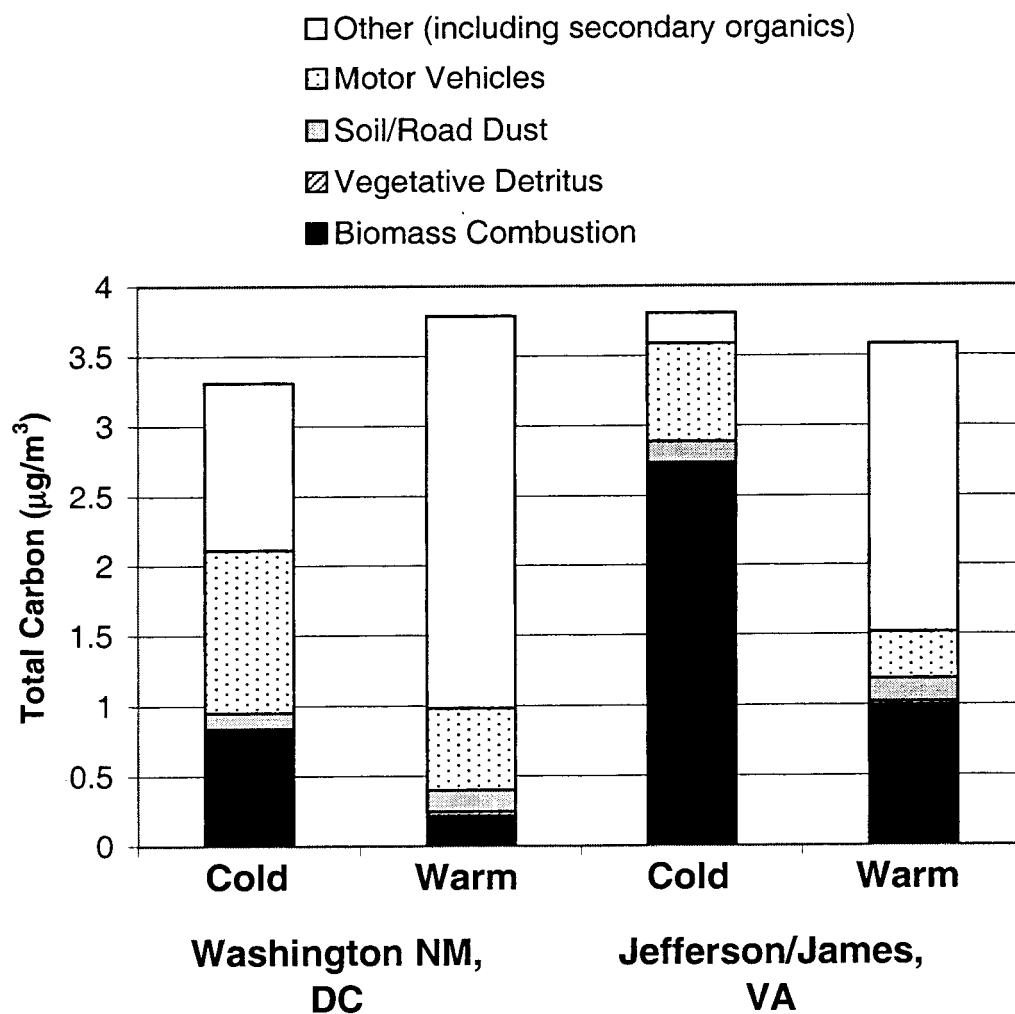


Figure 8.5. Source apportionment results for Washington DC and the Jefferson National Forest/James River Face Wilderness



and cold months, the biomass combustion contribution is less in the warm month samples. This suggests that the higher activity of residential wood combustion in colder weather makes a greater contribution to ambient particulate carbon than that of wildfires which occur primarily in the warm months. The relatively higher vehicular emissions in Washington DC are expected due to the more urban location of the sampling site. The higher “other” carbon contribution in the warm months might be due to more secondary organic aerosol formation caused by the higher solar irradiance in the warm seasons.

The contributions of biomass combustion to the fine particle total carbon concentrations at each of the IMPROVE and NESCAUM sites are shown geographically in Figures 8.6 and 8.7. During the colder months in the eastern states, roughly between 10 and 30% of the ambient fine particulate carbon is due to biomass combustion. The exceptions are located in rural mountainous areas where a greater degree of residential wood combustion is expected relative to other sources. Generally lower contributions from biomass combustion are observed in the southwestern states. In California and the Pacific Northwest, a wide range of contributions from biomass combustion are found. A possible explanation might be the influence of the non-uniform topography in the region. Biomass combustion sources and their influences on fine particle levels will tend to be more localized than the rest of the country with flatter terrain.

A comparison of Figures 8.6 and 8.7 clearly demonstrates that there is less of a biomass combustion contribution during the warm months than during the cold months. In the East, many of the sites show less than a 10% contribution from biomass combustion. The western states also show less biomass combustion while the Southwest remains at very low levels which are comparable to the warm month results. Since

Figure 8.6. The contributions of biomass combustion to the fine particle total carbon concentrations at each of the IMPROVE and NESCAUM sites in the cold month composite

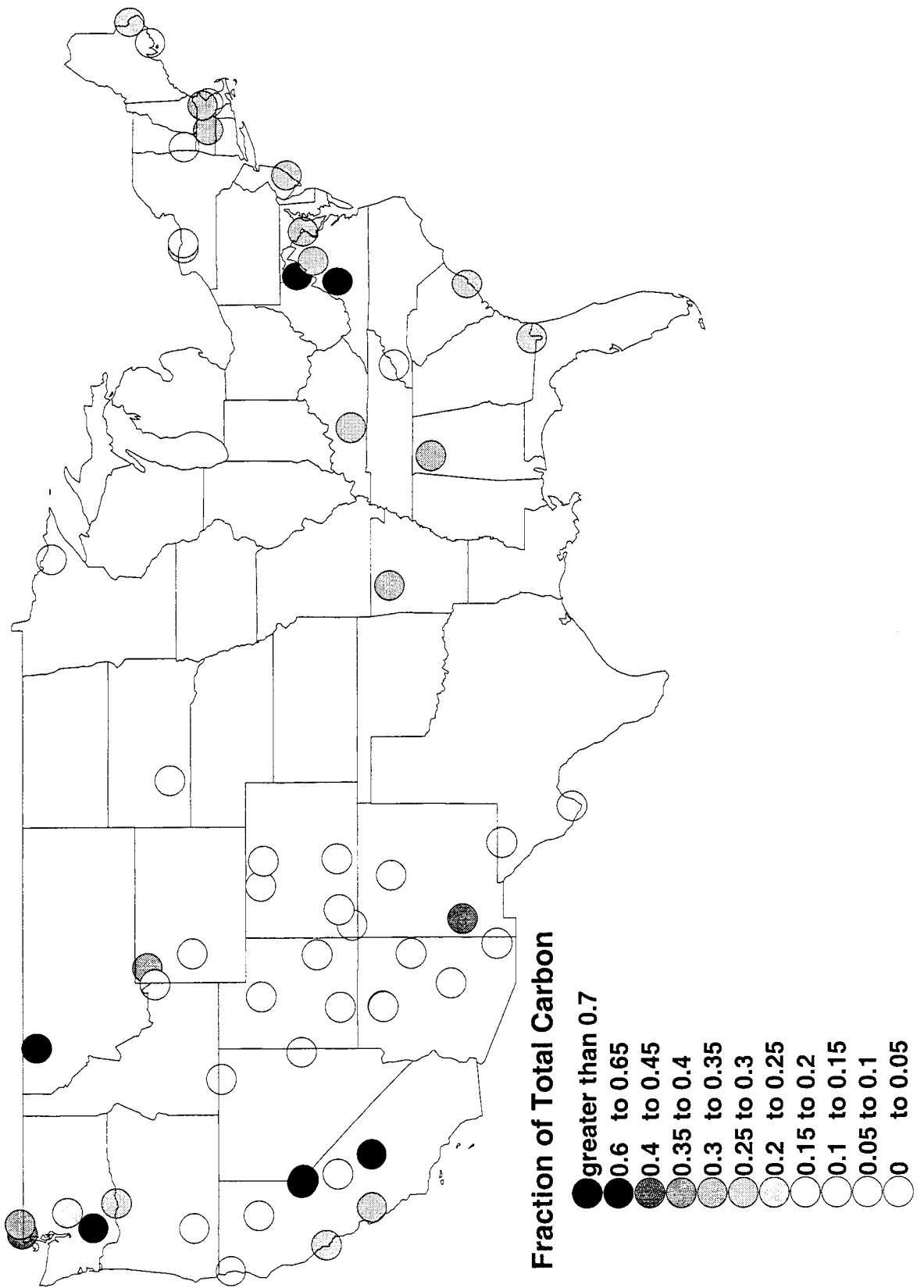
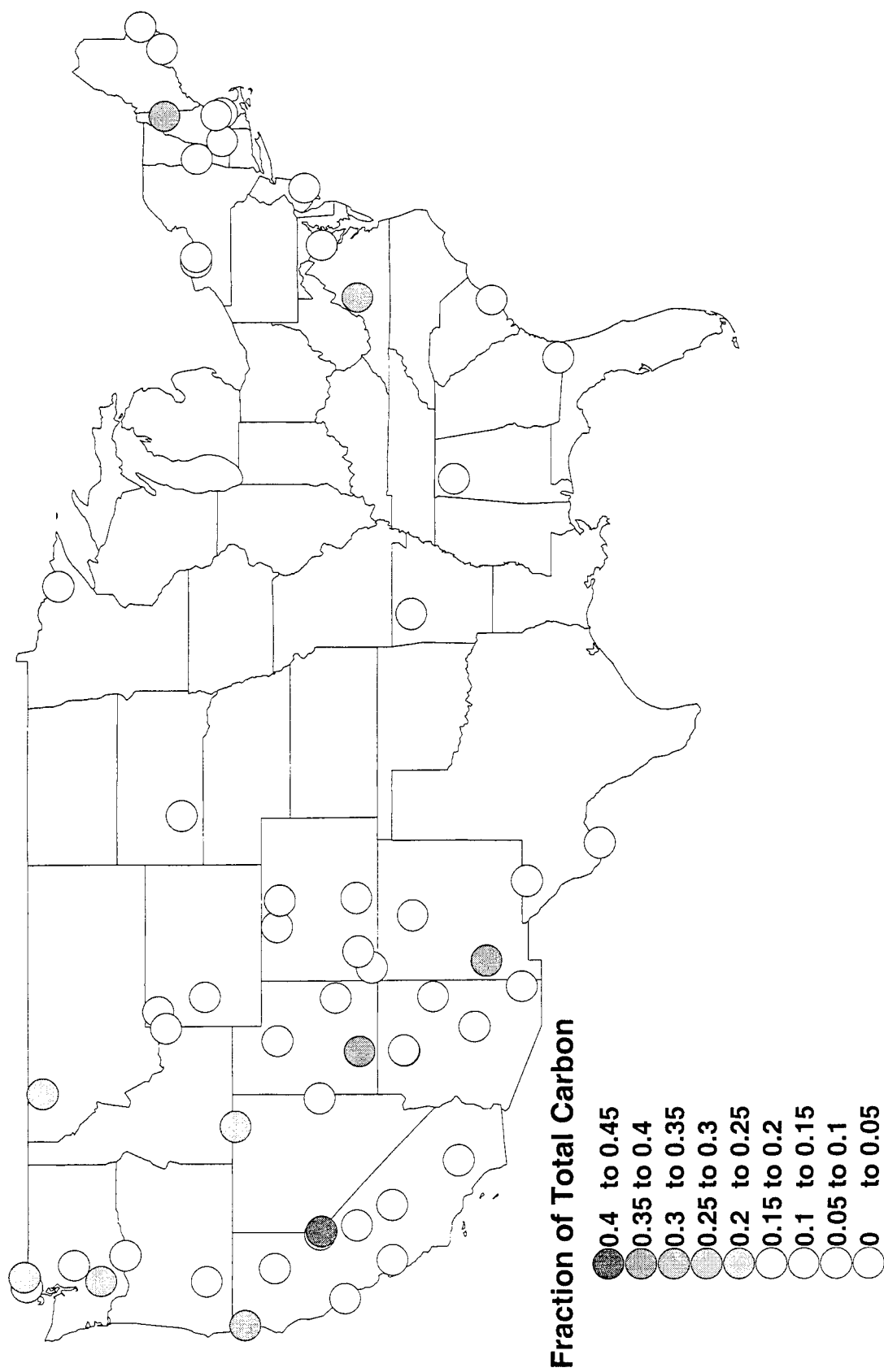


Figure 8.7. The contributions of biomass combustion to the fine particle total carbon concentrations at each of the IMPROVE and NESCAUM sites in the warm month composite



residential wood combustion activity is the primary source of biomass combustion in cold weather and forest fire activity occurs in the warmer seasons, the results suggest that residential wood combustion was a more important source of fine particulate carbon in 1995 than forest fires. Another possible reason for the lower biomass combustion contributions in the warm months was mentioned above with respect to Figure 8.6. The higher degree of solar irradiance in the warm seasons will lead to more secondary organic aerosol formation and thus, less of a contribution to total carbon from primary particle sources such as biomass combustion.

As a further validation of the model results, Figures 8.8 and 8.9 display the soil and road dust contributions to ambient fine particulate carbon at each of the sampling sites. In both the warm and cold month samples, much higher contributions from soil and road dust are seen in the southwestern states than the rest of the country. Given the dry and dusty conditions in this part of the country, one would expect more of a soil contribution to ambient particulate concentrations. Thus, the model results are reasonable with respect to this additional fine particle source.

8.4 Conclusions

The model results revealed several trends in the apportionment of fine particulate carbon in the United States. Biomass combustion is a more significant source in the colder months than in the warmer months, presumably due to the seasonality of residential wood combustion and forest fires. The amount of “other” carbon not accounted for by primary particle sources is higher in the warm months due to an

Figure 8.8. The contributions of soil/road dust to the fine particle total carbon concentrations at each of the IMPROVE and NESCAUM sites in the cold month composite

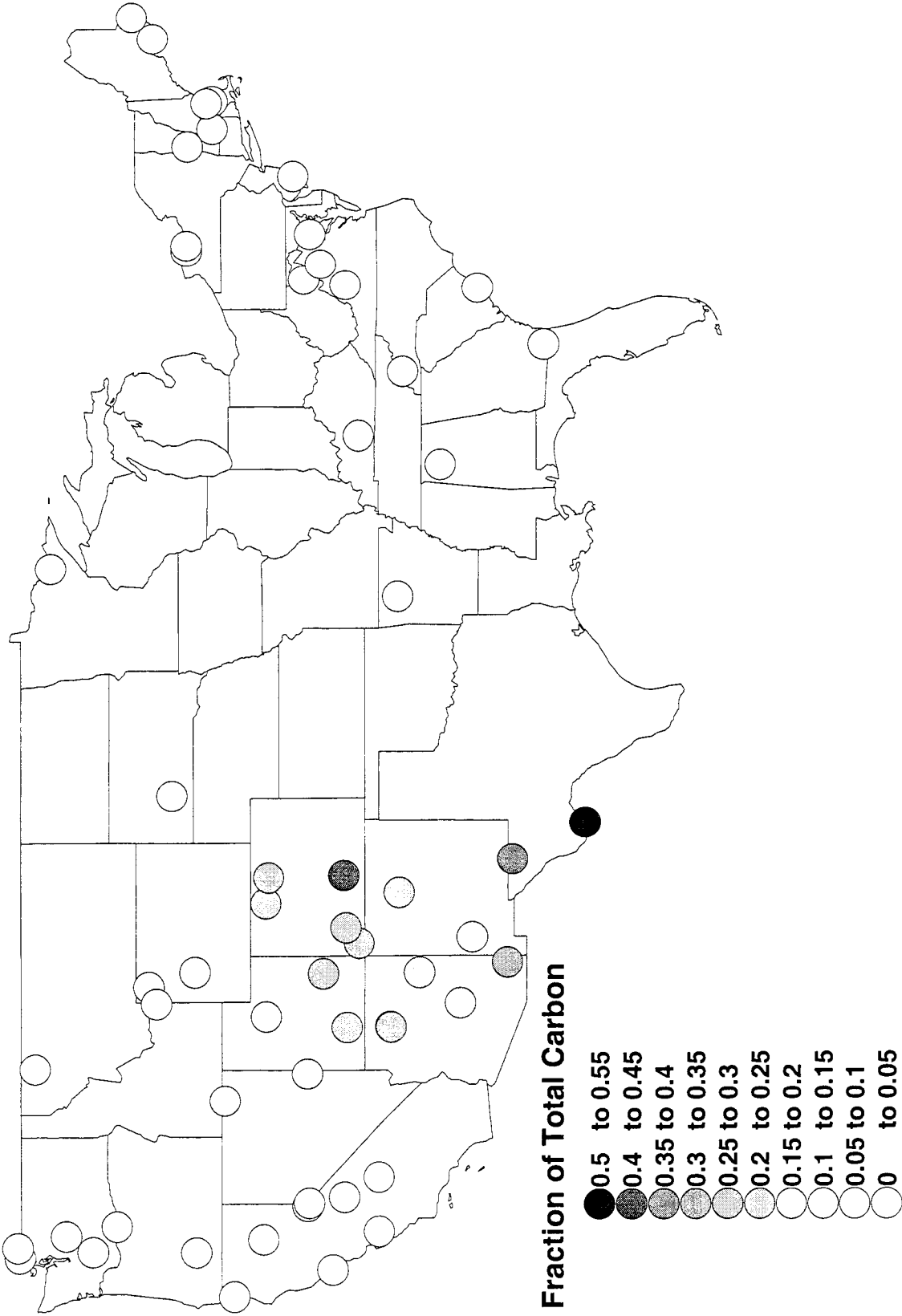
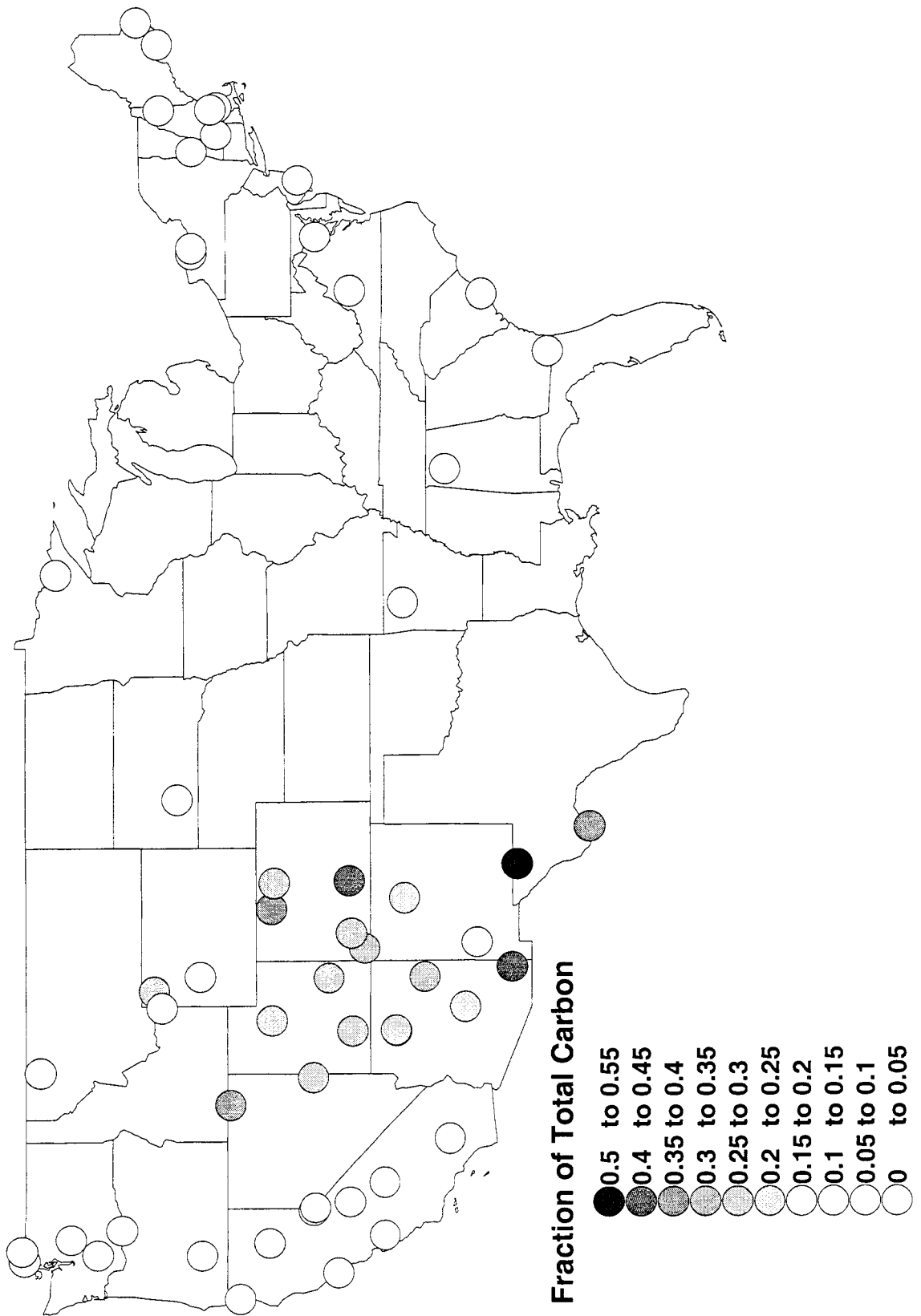


Figure 8.9. The contributions of soil/road dust to the fine particle total carbon concentrations at each of the IMPROVE and NESCAUM sites in the warm month composite



increased level of secondary organic aerosol formation. Finally, soil dust can be an important source of fine particle carbon in the dry areas of the Southwest U.S.

The current study should be considered a first attempt at a national source apportionment of ambient fine particle concentrations. While the results are consistent, reasonable, and provide some insight, several improvements are called for. With the exception of the residential wood combustion profiles, the source profiles used in the model calculations were derived from a very limited number of source tests conducted in California. The applicability of these profiles to other sampling locations needs to be investigated by additional source testing in other parts of the country. While the results for the forest fire samples were fairly consistent with our residential wood combustion profile, further testing is needed to determine the differences in emissions from other biomass combustion sources such as prescribed burning and agricultural burning. Hardwood and softwood combustion can also be considered as separate sources in the model due to some important differences in their organic compound emissions (4-8). Other fine particle carbon sources, such as meat cooking, could be added to future model calculations as well.

8.5 Acknowledgments

We thank Paul Mayo for his assistance in cutting the ambient filters samples; William Malm, Judy Chow, and DRI for providing the filters from the IMPROVE program; and Jamie Schauer for his guidance in using the chemical mass balance model. Financial support was provided by the U. S. Environmental Protection Agency under EPA Grant R826233-01-0 (California Institute of Technology).

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Appendix A

Results from the Organic Speciation of the Ambient Samples

The following tables display the results from the organic speciation of the ambient composite samples as analyzed by GC/MS. The organic compounds included in the tables represent those species thought potentially useful for future chemical mass balance calculations. The carbon, silicon, aluminum, and potassium results are taken from previous analyses performed on the filters by the Desert Research Institute.

Tables A.1 through A.4 are organized alphabetically by sampling site. All ambient concentrations are given in nanograms per cubic meter of each chemical species as measured across all of the sampling days for which filters were available. Cold month and warm month composite samples are included consecutively for each site, and individual filters from suspected wildfire days are also shown as indicated in the “Composite Sample” column. Values are not blank corrected. Zero values indicate that the species was not detected above detection limits. Uncertainties for the GC/MS quantification, and thus the concentration values in the tables, are approximately 20%.

Table A.1. Ambient Concentrations of Selected Fine Particle Chemical Species - Abbotsford to Chilliwack (all values in ng/m³)

Site	Composite Sample	Total Carbon	Silicon	Aluminum	Potassium	Guaiacyl Acetone	Acetovanillone	Vanillin	Syringaldehyde	Homovanillic Acid	Vanillic Acid	Sinapyl Aldehyde	Syringic Acid	Syringyl Acetone	Propionyl Syringol
Abbotsford, BC, Canada	Cold	2562	89	42	30	0.34	0.15	0.99	0.41	0.93	0.94	0.35	1.07	0.17	0.36
Abbotsford, BC, Canada	Warm	1906	106	59	24	0.07	0.02	0.43	0.19	0.00	0.00	0.00	0.00	0.07	0.00
Acadia NP, ME	Cold	927	33	15	22	0.03	0.03	0.13	0.45	0.00	0.23	0.00	0.00	0.06	0.16
Acadia NP, ME	Warm	1462	52	10	22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acadia NP, ME	8/23/95	16647	73	54	33	0.60	0.00	2.31	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Badlands NP, SD	Cold	596	59	25	9	0.00	0.00	0.10	0.32	0.00	0.00	0.00	0.00	0.00	0.08
Badlands NP, SD	Warm	1262	137	43	18	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bandelier NM, NM	Cold	732	104	41	9	0.02	0.05	0.22	0.22	0.00	0.00	0.00	0.00	0.00	0.03
Bandelier NM, NM	Warm	1011	175	53	12	0.02	0.03	0.14	0.05	0.00	0.33	0.00	0.00	0.00	0.00
Big Bend NP, TX	Cold	856	287	118	20	0.00	0.00	0.06	0.05	0.00	0.00	0.00	0.00	0.00	0.00
Big Bend NP, TX	Warm	1150	271	131	30	0.00	0.00	0.04	0.03	0.00	0.00	0.00	0.00	0.00	0.00
Bliss State Park, CA	Cold	543	38	19	7	0.17	0.16	0.39	0.11	0.35	0.74	0.00	0.00	0.05	0.03
Bliss State Park, CA	Warm	729	73	37	7	0.10	0.06	0.21	0.07	0.00	0.00	0.00	0.00	0.00	0.02
Boundary Waters Canoe Area, MN	Cold	594	39	15	10	0.00	0.00	0.07	0.14	0.00	0.00	0.00	0.00	0.00	0.03
Boundary Waters Canoe Area, MN	Warm	1479	52	19	15	0.00	0.00	0.07	0.05	0.00	0.00	0.00	0.00	0.00	0.00
Boundary Waters Canoe Area, MN	8/12/95	12307	42	29	56	5.30	1.03	5.10	0.00	0.00	0.00	0.00	0.00	0.58	0.00
Bridger Wilderness, WY	Cold	362	49	19	5	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bridger Wilderness, WY	Warm	842	95	30	22	0.04	0.00	0.10	0.16	0.00	0.00	0.00	0.00	0.00	0.04
Brigantine NWR, NJ	Cold	1974	65	31	21	0.06	0.04	0.38	0.31	0.00	0.50	0.00	2.15	0.00	0.60
Brigantine NWR, NJ	Warm	1990	90	27	19	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Brockport, NY	Cold	2673	88	29	0	0.00	0.00	1.99	0.00	0.00	0.00	0.00	0.00	0.05	0.00
Brockport, NY	Warm	3451	137	47	0	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bryce Canyon NP, UT	Cold	390	67	27	5	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bryce Canyon NP, UT	Warm	863	159	54	21	0.16	0.06	0.23	0.07	0.81	1.87	0.00	0.00	0.00	0.00
Canyonlands NP, UT	Cold	488	86	35	14	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Canyonlands NP, UT	Warm	731	160	48	24	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cape Romain NWR, SC	Cold	2380	67	31	47	0.10	0.03	0.25	0.16	0.00	0.00	0.00	1.84	0.15	0.18
Cape Romain NWR, SC	Warm	2023	166	92	36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chassahowitzka NWR, FL	Cold	2516	57	27	41	0.31	0.08	0.38	0.32	0.00	0.00	0.00	0.00	0.00	0.00
Chassahowitzka NWR, FL	Warm	2001	241	132	33	0.03	0.00	0.03	0.00	0.00	0.00	0.00	7.51	0.44	0.34
Chilliwack, BC, Canada	Cold	2405	123	51	32	0.26	0.08	0.87	0.31	0.00	0.72	0.00	0.00	0.10	0.44
Chilliwack, BC, Canada	Warm	2574	105	55	22	0.00	0.00	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A.1. Ambient Concentrations of Selected Fine Particle Chemical Species - Abbotsford to Chilliwack (all values in ng/m³)

Site	Composite Sample	Acetosyringone	Acetonylsyringol	Juvabione	Dehydrojuvabione	Beta-Sitosterol	Stigmast-4-en-3-one	Stigmasta-3,5-dien-7-one	Stigmasta-4,6-dien-3-one	Stigmastan-3-ol	Stigmastan-3-one	Friedelin	Beta-Amyrone	Beta-Amyrin	Alpha-Amyrone
Abbotsford, BC, Canada	Cold	0.76	0.23	0.06	0.00	1.43	0.32	0.15	0.00	0.26	0.07	0.00	0.03	0.04	0.06
Abbotsford, BC, Canada	Warm	0.07	0.08	0.12	0.00	0.00	0.08	0.05	0.00	0.10	0.05	0.12	0.02	0.02	0.03
Acadia NP, ME	Cold	0.39	0.09	0.00	0.00	0.08	0.05	0.04	0.00	0.04	0.03	0.00	0.00	0.00	0.00
Acadia NP, ME	Warm	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acadia NP, ME	8/23/95	0.00	0.00	3.02	0.54	0.00	1.38	0.64	0.00	0.00	1.65	2.77	0.18	0.15	0.51
Badlands NP, SD	Cold	0.19	0.05	0.00	0.00	0.00	0.03	0.01	0.00	0.05	0.03	0.00	0.00	0.00	0.00
Badlands NP, SD	Warm	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.05	0.00	0.00	0.00	0.00
Bandelier NM, NM	Cold	0.11	0.04	0.00	0.00	0.00	0.05	0.04	0.00	0.00	0.02	0.00	0.00	0.00	0.00
Bandelier NM, NM	Warm	0.04	0.00	0.00	0.00	0.00	0.05	0.02	0.00	0.00	0.02	0.06	0.00	0.00	0.00
Big Bend NP, TX	Cold	0.03	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00
Big Bend NP, TX	Warm	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.05	0.00	0.00	0.00
Bliss State Park, CA	Cold	0.10	0.07	0.00	0.00	0.25	0.16	0.08	0.00	0.07	0.05	0.05	0.00	0.00	0.00
Bliss State Park, CA	Warm	0.06	0.04	0.00	0.00	0.15	0.08	0.04	0.00	0.03	0.02	0.12	0.00	0.00	0.00
Boundary Waters Canoe Area, MN	Cold	0.12	0.00	0.00	0.00	0.00	0.03	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.01
Boundary Waters Canoe Area, MN	Warm	0.04	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.02	0.02	0.00	0.00	0.00
Boundary Waters Canoe Area, MN	8/12/95	0.00	0.89	4.62	0.43	0.00	3.72	3.11	0.00	2.31	2.36	0.00	0.41	0.41	0.69
Bridger Wilderness, WY	Cold	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bridger Wilderness, WY	Warm	0.14	0.08	0.00	0.00	0.07	0.03	0.02	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Brigantine NWR, NJ	Cold	1.32	0.04	0.00	0.00	0.00	0.08	0.05	0.00	0.07	0.00	0.51	0.01	0.01	0.01
Brigantine NWR, NJ	Warm	0.00	0.00	0.00	0.00	0.00	0.04	0.03	0.00	0.00	0.00	0.18	0.01	0.00	0.02
Brockport, NY	Cold	0.00	0.00	0.00	0.00	0.35	0.18	0.05	0.03	0.15	0.03	0.30	0.02	0.02	0.02
Brockport, NY	Warm	0.00	0.00	0.00	0.00	0.00	0.05	0.03	0.00	0.00	0.00	0.16	0.00	0.00	0.00
Bryce Canyon NP, UT	Cold	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bryce Canyon NP, UT	Warm	0.05	0.00	0.00	0.00	0.30	0.13	0.08	0.03	0.05	0.05	0.00	0.00	0.00	0.02
Canyonlands NP, UT	Cold	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Canyonlands NP, UT	Warm	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cape Romain NWR, SC	Cold	0.30	0.17	0.00	0.00	0.20	0.29	0.08	0.04	0.09	0.02	0.52	0.02	0.03	0.04
Cape Romain NWR, SC	Warm	0.00	0.00	0.00	0.00	0.00	0.11	0.07	0.00	0.00	0.00	0.28	0.02	0.00	0.10
Chassahowitzka NWR, FL	Cold	0.53	0.56	0.00	0.00	0.29	0.44	0.13	0.06	0.11	0.06	0.71	0.04	0.04	0.10
Chassahowitzka NWR, FL	Warm	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chilliwack, BC, Canada	Cold	0.96	0.11	0.00	0.00	0.76	0.36	0.13	0.06	0.25	0.04	0.15	0.02	0.02	0.04
Chilliwack, BC, Canada	Warm	0.00	0.00	0.14	0.00	0.37	0.19	0.05	0.00	0.10	0.05	0.00	0.02	0.01	0.03

Table A.1. Ambient Concentrations of Selected Fine Particle Chemical Species - Abbotstford to Chilliwack (all values in ng/m³)

Site	Composite Sample	Alpha-Amyrin	Alpha-Tocopherol	Delta-Tocopherol	Beta-Tocopherol	Betulin	Cholesterol	Hexadecane	Heptadecane	Octadecane	Nonadecane	Eicosane	Henelicosane	Docosane	Tricosane
Abbotsford, BC, Canada	Cold	0.10	0.00	0.00	0.00	0.00	0.69	0.22	0.00	0.00	0.00	0.00	0.12	0.19	0.39
Abbotsford, BC, Canada	Warm	0.04	0.00	0.00	0.00	0.00	1.33	0.66	0.18	0.00	0.00	0.00	0.00	2.70	0.29
Acadia NP, ME	Cold	0.01	0.00	0.00	0.00	0.23	0.31	0.00	0.00	0.00	0.00	0.07	0.10	0.17	0.29
Acadia NP, ME	Warm	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.02	0.00	0.00	0.04	0.04	0.08	0.19
Acadia NP, ME	8/23/95	0.41	0.00	0.00	0.00	0.00	6.06	2.78	0.89	0.00	0.00	0.00	0.00	0.79	1.38
Badlands NP,SD	Cold	0.00	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.00	0.00	0.08	0.12	0.16	0.25
Badlands NP,SD	Warm	0.01	0.00	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.12	0.15	0.12	0.20
Bandelier NM, NM	Cold	0.00	0.00	0.00	0.00	0.00	0.23	0.00	0.00	0.00	0.00	0.08	0.15	0.23	0.33
Bandelier NM, NM	Warm	0.00	0.00	0.00	0.00	0.00	0.20	0.00	0.00	0.00	0.00	0.00	0.11	0.14	0.25
Big Bend NP, TX	Cold	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.07	0.11	0.17	0.28
Big Bend NP, TX	Warm	0.00	0.00	0.00	0.00	0.00	0.71	0.00	0.00	0.00	0.00	0.08	0.17	0.27	0.39
Bliss State Park, CA	Cold	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.10	0.17	0.17	0.31
Bliss State Park, CA	Warm	0.00	0.00	0.00	0.00	0.00	0.19	0.00	0.00	0.12	0.19	0.14	0.20	0.25	0.33
Boundary Waters Canoe Area, MN	Cold	0.00	0.00	0.00	0.00	0.00	0.33	0.00	0.00	0.00	0.00	0.10	0.15	0.22	0.58
Boundary Waters Canoe Area, MN	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.62	1.74
Boundary Waters Canoe Area, MN	8/12/95	0.75	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.33
Bridger Wilderness, WY	Cold	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.08	0.13	0.19	0.33
Bridger Wilderness, WY	Warm	0.00	0.00	0.00	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.08	0.16	0.21	0.67
Brigantine NWR, NJ	Cold	0.02	0.00	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.05	0.10	0.21	0.40
Brigantine NWR, NJ	Warm	0.01	0.00	0.00	0.00	0.00	0.14	0.02	0.00	0.00	0.00	0.05	0.05	0.10	0.19
Brockport, NY	Cold	0.02	0.00	0.00	0.00	0.00	0.97	0.00	0.19	0.27	0.41	0.45	0.66	0.93	1.26
Brockport, NY	Warm	0.00	0.00	0.00	0.00	0.00	0.73	0.00	0.23	0.00	0.16	0.21	0.45	0.48	0.94
Bryce Canyon NP, UT	Cold	0.00	0.00	0.00	0.00	0.00	0.16	4.85	0.00	0.00	0.00	0.09	0.15	0.19	0.23
Bryce Canyon NP, UT	Warm	0.02	0.00	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.00	0.05	0.07	0.13	0.28
Canyonlands NP, UT	Cold	0.00	0.00	0.00	0.00	0.00	0.13	5.32	0.00	0.06	0.00	0.10	0.15	0.19	0.34
Canyonlands NP, UT	Warm	0.00	0.00	0.00	0.00	0.00	0.17	7.00	0.01	0.00	0.04	0.05	0.09	0.15	0.40
Cape Romain NWR, SC	Cold	0.06	0.02	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.06	0.09	0.16	0.32
Cape Romain NWR, SC	Warm	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.04	0.07	0.14	0.29
Chassahowitzka NWR, FL	Cold	0.08	0.10	0.00	0.00	0.00	0.21	2.20	0.01	0.00	0.02	0.07	0.09	0.16	0.31
Chassahowitzka NWR, FL	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.01	0.11	0.04	0.06	0.15
Chilliwack, BC, Canada	Cold	0.06	0.06	0.00	0.00	0.00	0.22	0.00	0.01	0.00	0.04	0.06	0.11	0.20	0.38
Chilliwack, BC, Canada	Warm	0.03	0.00	0.00	0.00	0.00	0.33	5.55	0.00	0.00	0.09	0.08	0.09	0.16	0.32

Table A.1. Ambient Concentrations of Selected Fine Particle Chemical Species - Abbotsford to Chilliwack (all values in ng/m³)

Site	Composite Sample	Tetracosane	Pentacosane	Hexacosane	Heptacosane	Octacosane	Nonacosane	Triacosane	hentriacontane	Dotriacontane	Tritriacontane	Tetratriacontane	Pentatriacontane	Hexatriacontane	Fluoranthene
Abbotsford, BC, Canada	Cold	0.57	1.04	0.88	1.13	0.63	1.13	0.55	0.69	0.33	0.40	0.66	0.52	0.00	0.028
Abbotsford, BC, Canada	Warm	0.49	0.74	0.63	1.10	0.62	1.33	0.50	0.66	0.36	0.36	0.00	0.00	0.00	0.013
Acadia NP, ME	Cold	0.46	0.49	0.37	0.43	0.23	0.37	0.18	0.23	0.14	0.00	0.00	0.00	0.00	0.038
Acadia NP, ME	Warm	0.31	0.69	0.40	0.65	0.24	0.47	0.17	0.38	0.11	0.11	0.00	0.00	0.00	0.005
Acadia NP, ME	8/23/95	2.17	7.13	7.12	20.95	6.55	11.81	3.56	9.98	1.89	4.00	0.00	0.00	0.00	0.060
Badlands NP, SD	Cold	0.31	0.33	0.23	0.30	0.14	0.43	0.10	0.29	0.00	0.08	0.00	0.00	0.00	0.008
Badlands NP, SD	Warm	0.39	0.77	0.54	1.13	0.44	3.20	0.32	2.68	0.16	0.57	0.00	0.00	0.00	0.003
Bandelier NM, NM	Cold	0.39	0.36	0.27	0.33	0.19	0.37	0.15	0.26	0.09	0.10	0.00	0.00	0.00	0.019
Bandelier NM, NM	Warm	0.44	0.45	0.38	0.50	0.27	0.67	0.17	0.45	0.10	0.19	0.06	0.06	0.00	0.006
Big Bend NP, TX	Cold	0.45	0.50	0.38	0.54	0.28	0.70	0.20	0.66	0.15	0.28	0.08	0.07	0.00	0.012
Big Bend NP, TX	Warm	0.38	0.53	0.51	0.00	0.46	0.96	0.31	0.71	0.21	0.28	0.15	0.12	0.00	0.010
Bliss State Park, CA	Cold	0.39	0.38	0.25	0.45	0.19	0.48	0.14	0.25	0.06	0.10	0.00	0.00	0.00	0.008
Bliss State Park, CA	Warm	0.38	0.62	0.30	0.61	0.19	0.81	0.14	0.36	0.07	0.11	0.00	0.00	0.00	0.005
Boundary Waters Canoe Area, MN	Cold	0.31	0.38	0.22	0.37	0.16	0.33	0.14	0.21	0.11	0.00	0.00	0.00	0.00	0.016
Boundary Waters Canoe Area, MN	Warm	0.41	1.26	0.47	1.25	0.30	0.98	0.23	0.77	0.18	0.27	0.00	0.00	0.00	0.004
Boundary Waters Canoe Area, MN	8/12/95	0.97	3.78	1.60	12.36	2.04	6.35	0.86	4.27	0.58	1.51	0.00	0.00	0.00	0.000
Bridger Wilderness, WY	Cold	0.40	0.35	0.24	0.24	0.13	0.20	0.09	0.15	0.05	0.04	0.00	0.00	0.00	0.005
Bridger Wilderness, WY	Warm	0.53	0.99	0.43	0.73	0.29	0.94	0.23	0.54	0.14	0.17	0.07	0.08	0.00	0.004
Brigantine NWR, NJ	Cold	0.68	0.84	0.49	0.59	0.37	0.72	0.27	0.48	0.15	0.21	0.00	0.00	0.00	0.058
Brigantine NWR, NJ	Warm	0.24	0.61	0.46	0.94	0.40	1.07	0.28	0.68	0.17	0.22	0.00	0.00	0.00	0.013
Brockport, NY	Cold	1.56	2.48	3.14	3.61	3.17	3.20	2.18	2.02	1.08	0.77	0.49	0.26	0.14	0.293
Brockport, NY	Warm	1.30	2.53	2.45	3.54	2.44	3.24	1.71	2.25	0.85	0.80	0.34	0.21	0.13	0.097
Bryce Canyon NP, UT	Cold	0.21	0.22	0.15	0.16	0.10	0.22	0.09	0.14	0.00	0.00	0.00	0.00	0.00	0.004
Bryce Canyon NP, UT	Warm	0.52	0.68	0.34	0.45	0.23	0.91	0.16	0.53	0.07	0.23	0.00	0.00	0.00	0.006
Canyonlands NP, UT	Cold	0.45	0.42	0.23	0.28	0.20	0.32	0.14	0.21	0.08	0.07	0.00	0.00	0.00	0.009
Canyonlands NP, UT	Warm	0.95	1.28	0.87	0.89	0.62	1.17	0.41	0.74	0.32	0.28	0.20	0.13	0.00	0.004
Cape Romain NWR, SC	Cold	0.40	0.57	0.46	0.49	0.36	0.89	0.28	0.67	0.17	0.21	0.08	0.10	0.00	0.036
Cape Romain NWR, SC	Warm	0.29	0.33	0.00	0.56	0.46	0.91	0.45	0.74	0.37	0.31	0.20	0.17	0.08	0.008
Chassahowitzka NWR, FL	Cold	0.59	0.71	0.50	0.53	0.48	0.92	0.43	0.79	0.25	0.37	0.23	0.19	0.00	0.020
Chassahowitzka NWR, FL	Warm	0.28	0.35	0.33	0.70	0.51	0.91	0.40	0.66	0.28	0.28	0.17	0.15	0.00	0.008
Chilliwack, BC, Canada	Cold	0.66	1.03	0.58	0.80	0.41	0.80	0.37	0.60	0.25	0.25	0.23	0.21	0.00	0.021
Chilliwack, BC, Canada	Warm	0.40	0.81	0.47	0.80	0.37	0.72	0.32	0.65	0.19	0.27	0.00	0.00	0.00	0.012

Table A.1. Ambient Concentrations of Selected Fine Particle Chemical Species - Abbotsford to Chilliwack (all values in ng/m³)

Site	Composite Sample	Acphenanthrylene	Pyrene	Retene	Benzo(ghi)fluoranthene	Cyclopenta(cd)pyrene	Benz(a)anthracene	Chrysene/Triphenylene	Benzo(k)fluoranthene	Benzo(b)fluoranthene	Benzo(i)fluoranthene	Benzo(e)pyrene	Benzo(a)pyrene	Perylene	Indeno(cd)pyrene
Abbotsford, BC, Canada	Cold	0.012	0.042	0.128	0.034	0.019	0.042	0.087	0.175	0.198	0.036	0.165	0.146	0.028	0.200
Abbotsford, BC, Canada	Warm	0.004	0.015	0.033	0.009	0.004	0.007	0.019	0.041	0.052	0.000	0.053	0.029	0.000	0.056
Acadia NP, ME	Cold	0.006	0.040	0.020	0.017	0.005	0.013	0.058	0.058	0.117	0.005	0.074	0.030	0.004	0.059
Acadia NP, ME	Warm	0.001	0.005	0.000	0.003	0.001	0.001	0.005	0.005	0.015	0.000	0.011	0.002	0.001	0.008
Acadia NP, ME	8/23/95	0.000	0.066	0.365	0.000	0.000	0.083	0.062	0.000	0.109	0.000	0.073	0.000	0.000	0.063
Badlands NP,SD	Cold	0.000	0.010	0.017	0.005	0.002	0.003	0.008	0.010	0.014	0.000	0.012	0.000	0.000	0.007
Badlands NP,SD	Warm	0.000	0.005	0.008	0.003	0.000	0.000	0.002	0.002	0.005	0.000	0.013	0.000	0.000	0.003
Bandelier NM, NM	Cold	0.004	0.020	0.170	0.012	0.003	0.008	0.019	0.029	0.025	0.006	0.024	0.016	0.005	0.023
Bandelier NM, NM	Warm	0.000	0.008	0.105	0.004	0.000	0.003	0.006	0.014	0.015	0.000	0.010	0.004	0.000	0.007
Big Bend NP, TX	Cold	0.002	0.013	0.014	0.005	0.002	0.002	0.009	0.009	0.011	0.002	0.011	0.006	0.000	0.007
Big Bend NP, TX	Warm	0.000	0.011	0.000	0.005	0.000	0.002	0.014	0.008	0.009	0.000	0.011	0.006	0.000	0.006
Bliss State Park, CA	Cold	0.003	0.010	0.258	0.011	0.000	0.005	0.016	0.022	0.025	0.005	0.022	0.010	0.000	0.019
Bliss State Park, CA	Warm	0.002	0.007	0.073	0.004	0.001	0.002	0.004	0.006	0.007	0.000	0.009	0.004	0.000	0.006
Boundary Waters Canoe Area, MN	Cold	0.003	0.015	0.029	0.009	0.002	0.005	0.016	0.024	0.025	0.000	0.020	0.008	0.000	0.019
Boundary Waters Canoe Area, MN	Warm	0.000	0.005	0.018	0.008	0.000	0.000	0.004	0.006	0.006	0.000	0.009	0.004	0.007	0.005
Boundary Waters Canoe Area, MN	8/12/95	0.000	0.000	0.654	0.251	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.149
Bridger Wilderness, WY	Cold	0.000	0.007	0.020	0.004	0.000	0.002	0.004	0.004	0.005	0.000	0.006	0.000	0.000	0.003
Bridger Wilderness, WY	Warm	0.001	0.007	0.014	0.007	0.001	0.007	0.018	0.013	0.017	0.002	0.024	0.007	0.000	0.010
Brigantine NWR, NJ	Cold	0.008	0.057	0.044	0.028	0.008	0.024	0.075	0.110	0.162	0.013	0.110	0.067	0.014	0.106
Brigantine NWR, NJ	Warm	0.001	0.013	0.010	0.006	0.001	0.003	0.011	0.010	0.020	0.000	0.018	0.007	0.001	0.014
Brockport, NY	Cold	0.014	0.180	0.047	0.093	0.009	0.046	0.274	0.282	0.278	0.000	0.228	0.055	0.008	0.124
Brockport, NY	Warm	0.007	0.056	0.000	0.023	0.006	0.016	0.084	0.102	0.090	0.000	0.093	0.033	0.000	0.057
Bryce Canyon NP, UT	Cold	0.001	0.005	0.026	0.003	0.000	0.001	0.003	0.005	0.004	0.000	0.005	0.000	0.000	0.002
Bryce Canyon NP, UT	Warm	0.002	0.011	3.754	0.017	0.006	0.022	0.041	0.026	0.021	0.005	0.021	0.017	0.005	0.015
Canyonlands NP, UT	Cold	0.001	0.009	0.022	0.005	0.001	0.002	0.006	0.007	0.009	0.000	0.009	0.004	0.000	0.004
Canyonlands NP, UT	Warm	0.000	0.006	0.011	0.004	0.000	0.000	0.003	0.002	0.005	0.000	0.010	0.000	0.000	0.002
Cape Romain NWR, SC	Cold	0.006	0.036	0.057	0.019	0.004	0.011	0.035	0.075	0.091	0.006	0.081	0.029	0.006	0.065
Cape Romain NWR, SC	Warm	0.000	0.011	0.010	0.010	0.000	0.000	0.003	0.009	0.009	0.000	0.019	0.003	0.000	0.010
Chassahowitzka NWR, FL	Cold	0.005	0.024	0.058	0.013	0.006	0.013	0.033	0.070	0.071	0.007	0.075	0.042	0.007	0.090
Chassahowitzka NWR, FL	Warm	0.000	0.011	0.012	0.005	0.001	0.002	0.009	0.011	0.014	0.001	0.017	0.007	0.002	0.020
Chilliwack, BC, Canada	Cold	0.008	0.032	0.057	0.031	0.010	0.029	0.071	0.168	0.187	0.018	0.153	0.097	0.015	0.157
Chilliwack, BC, Canada	Warm	0.002	0.023	0.034	0.010	0.003	0.009	0.024	0.052	0.048	0.000	0.058	0.030	0.005	0.056

Table A.1. Ambient Concentrations of Selected Fine Particle Chemical Species - Abbotstford to Chilliwack (all values in ng/m³)

Site	Composite Sample	Benzo(ghi)perylene	Indeno(1,2,3-cd)fluoranthene	Dibenz[a,h]anthracene	Coronene	22,29,30-Trisnorhopane	22,29,30-Trisnorhopane	17a(H)-21b(H)-29-Norhopane	18a(H)-29-Norhopane	17b(H)-21a(H)-Normoretane	17a(H)-21b(H)-Hopane	17b(H),21a(H)-Moretane	22S, 17a(H),21b(H)-Homohopane	22R, 17a(H),21b(H)-Homohopane	22S, 17a(H),21b(H)-Bishomohopane
Abbotsford, BC, Canada	Cold	0.284	0.072	0.029	0.769	0.039	0.046	0.179	0.033	0.036	0.244	0.000	0.104	0.078	0.074
Abbotsford, BC, Canada	Warm	0.085	0.019	0.009	0.256	0.000	0.000	0.100	0.000	0.187	0.112	0.000	0.088	0.059	0.053
Acadia NP, ME	Cold	0.067	0.020	0.008	0.169	0.013	0.016	0.085	0.019	0.000	0.082	0.000	0.052	0.040	0.031
Acadia NP, ME	Warm	0.013	0.003	0.001	0.040	0.015	0.018	0.087	0.023	0.022	0.097	0.007	0.048	0.035	0.032
Acadia NP, ME	8/23/95	0.042	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Badlands NP,SD	Cold	0.012	0.004	0.002	0.044	0.000	0.000	0.026	0.000	0.000	0.043	0.000	0.000	0.000	0.000
Badlands NP,SD	Warm	0.007	0.000	0.000	0.026	0.009	0.009	0.041	0.011	0.000	0.058	0.009	0.022	0.020	0.012
Bandelier NM, NM	Cold	0.027	0.010	0.004	0.079	0.013	0.000	0.037	0.009	0.000	0.055	0.000	0.014	0.018	0.012
Bandelier NM, NM	Warm	0.010	0.002	0.001	0.040	0.012	0.011	0.041	0.013	0.000	0.055	0.000	0.023	0.019	0.012
Big Bend NP, TX	Cold	0.010	0.002	0.000	0.035	0.016	0.017	0.065	0.014	0.000	0.064	0.000	0.026	0.023	0.015
Big Bend NP, TX	Warm	0.010	0.002	0.001	0.033	0.012	0.018	0.052	0.016	0.000	0.065	0.000	0.032	0.026	0.021
Bliss State Park, CA	Cold	0.021	0.008	0.003	0.069	0.011	0.017	0.038	0.010	0.000	0.041	0.000	0.025	0.021	0.000
Bliss State Park, CA	Warm	0.009	0.003	0.000	0.041	0.016	0.010	0.049	0.021	0.000	0.059	0.000	0.024	0.026	0.014
Boundary Waters Canoe Area, MN	Cold	0.019	0.007	0.003	0.062	0.019	0.021	0.095	0.018	0.000	0.109	0.015	0.068	0.056	0.055
Boundary Waters Canoe Area, MN	Warm	0.008	0.002	0.000	0.036	0.017	0.017	0.113	0.022	0.000	0.112	0.013	0.069	0.058	0.050
Boundary Waters Canoe Area, MN	8/12/95	0.154	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Bridger Wilderness, WY	Cold	0.008	0.002	0.000	0.027	0.005	0.011	0.027	0.009	0.000	0.041	0.007	0.017	0.013	0.000
Bridger Wilderness, WY	Warm	0.021	0.004	0.003	0.039	0.011	0.018	0.045	0.013	0.000	0.054	0.000	0.022	0.021	0.015
Brigantine NWR, NJ	Cold	0.150	0.040	0.015	0.320	0.021	0.025	0.102	0.039	0.000	0.130	0.000	0.061	0.038	0.034
Brigantine NWR, NJ	Warm	0.026	0.005	0.002	0.076	0.009	0.011	0.048	0.017	0.000	0.069	0.009	0.034	0.026	0.022
Brockport, NY	Cold	0.187	0.054	0.014	0.381	0.045	0.034	0.140	0.029	0.000	0.160	0.013	0.050	0.044	0.031
Brockport, NY	Warm	0.086	0.026	0.000	0.200	0.035	0.000	0.136	0.000	0.000	0.216	0.000	0.051	0.057	0.000
Bryce Canyon NP, UT	Cold	0.006	0.000	0.000	0.019	0.008	0.009	0.031	0.011	0.000	0.040	0.000	0.017	0.015	0.009
Bryce Canyon NP, UT	Warm	0.019	0.007	0.003	0.040	0.013	0.014	0.041	0.011	0.000	0.051	0.000	0.022	0.014	0.010
Canyonlands NP, UT	Cold	0.010	0.002	0.000	0.028	0.007	0.009	0.027	0.009	0.000	0.032	0.006	0.009	0.008	0.000
Canyonlands NP, UT	Warm	0.011	0.001	0.000	0.031	0.012	0.010	0.037	0.010	0.000	0.051	0.005	0.018	0.015	0.009
Cape Romain NWR, SC	Cold	0.089	0.028	0.010	0.181	0.010	0.013	0.054	0.016	0.000	0.076	0.000	0.031	0.028	0.019
Cape Romain NWR, SC	Warm	0.026	0.004	0.002	0.067	0.008	0.007	0.032	0.009	0.000	0.047	0.005	0.023	0.019	0.014
Chassahowitzka NWR, FL	Cold	0.133	0.037	0.013	0.330	0.017	0.026	0.086	0.028	0.000	0.135	0.015	0.079	0.084	0.047
Chassahowitzka NWR, FL	Warm	0.037	0.009	0.003	0.119	0.014	0.008	0.041	0.014	0.000	0.085	0.000	0.044	0.039	0.031
Chilliwack, BC, Canada	Cold	0.230	0.063	0.020	0.519	0.030	0.042	0.137	0.042	0.000	0.209	0.021	0.098	0.084	0.070
Chilliwack, BC, Canada	Warm	0.102	0.025	0.005	0.306	0.016	0.017	0.077	0.026	0.000	0.113	0.000	0.059	0.050	0.043

Table A.1. Ambient Concentrations of Selected Fine Particle Chemical Species - Abbotstford to Chilliwack (all values in ng/m³)

Site	Composite Sample	22R, 17a(H),21b(H)- Bishomohopane	22S, 17a(H),21b(H)- Trishomohopane	22R, 17a(H),21b(H)- Trishomohopane	20R+S, abb-Cholestane	20R, aaa-Cholestane	20R+S, abb-Ergostane	20R+S, abb-Sitostane	1H-Phenalen-1-one	Anthracen-9,10-dione	Benz(de)anthracen-7-one	Benz(a)anthracen-7,12-dione	Dibenzofuran	Squalene	Nonanal
Abbotsford, BC, Canada	Cold	0.056	0.050	0.033	0.126	0.114	0.082	0.120	0.057	0.034	0.354	0.114	0.00	1.40	0.37
Abbotsford, BC, Canada	Warm	0.000	0.036	0.000	0.095	0.075	0.033	0.074	0.000	0.000	0.054	0.033	0.00	3.03	1.00
Acadia NP, ME	Cold	0.021	0.023	0.010	0.028	0.025	0.000	0.034	0.019	0.021	0.076	0.044	0.00	0.69	0.21
Acadia NP, ME	Warm	0.021	0.024	0.017	0.024	0.025	0.000	0.032	0.000	0.000	0.000	0.000	0.00	1.50	0.00
Acadia NP, ME	8/23/95	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00	13.89	0.00
Badlands NP, SD	Cold	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.011	0.014	0.000	0.00	0.51	0.00
Badlands NP, SD	Warm	0.010	0.013	0.000	0.018	0.011	0.000	0.018	0.000	0.000	0.000	0.000	0.00	0.52	0.29
Bandelier NM, NM	Cold	0.011	0.000	0.000	0.016	0.015	0.000	0.020	0.018	0.015	0.049	0.017	0.00	0.72	0.30
Bandelier NM, NM	Warm	0.012	0.000	0.000	0.000	0.016	0.000	0.023	0.000	0.000	0.009	0.000	0.00	0.57	0.19
Big Bend NP, TX	Cold	0.013	0.009	0.010	0.030	0.017	0.000	0.026	0.000	0.007	0.008	0.000	0.00	0.55	0.14
Big Bend NP, TX	Warm	0.020	0.012	0.010	0.020	0.007	0.000	0.025	0.000	0.000	0.005	0.000	0.00	0.42	0.00
Bliss State Park, CA	Cold	0.000	0.000	0.000	0.000	0.012	0.000	0.000	0.010	0.015	0.029	0.011	0.00	0.80	0.36
Bliss State Park, CA	Warm	0.014	0.011	0.000	0.018	0.018	0.000	0.019	0.000	0.009	0.008	0.000	0.00	0.40	0.33
Boundary Waters Canoe Area, MN	Cold	0.039	0.043	0.026	0.029	0.020	0.000	0.040	0.009	0.016	0.032	0.019	0.00	0.56	0.00
Boundary Waters Canoe Area, MN	Warm	0.043	0.035	0.031	0.028	0.016	0.000	0.033	0.000	0.000	0.006	0.000	0.00	1.25	0.00
Boundary Waters Canoe Area, MN	8/12/95	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.17	3.45	0.00
Bridger Wilderness, WY	Cold	0.000	0.000	0.000	0.017	0.013	0.000	0.017	0.000	0.000	0.000	0.000	0.00	0.67	0.31
Bridger Wilderness, WY	Warm	0.014	0.010	0.000	0.024	0.015	0.000	0.022	0.000	0.000	0.011	0.000	0.00	0.36	0.19
Brigantine NWR, NJ	Cold	0.023	0.021	0.015	0.050	0.052	0.000	0.064	0.028	0.040	0.188	0.101	0.00	0.67	0.13
Brigantine NWR, NJ	Warm	0.014	0.014	0.010	0.019	0.009	0.000	0.026	0.000	0.000	0.013	0.000	0.00	0.33	0.40
Brockport, NY	Cold	0.025	0.020	0.000	0.080	0.060	0.034	0.081	0.041	0.235	0.124	0.088	0.00	0.59	0.00
Brockport, NY	Warm	0.000	0.000	0.000	0.000	0.050	0.000	0.091	0.000	0.141	0.000	0.000	0.00	1.23	12.96
Bryce Canyon NP, UT	Cold	0.011	0.000	0.000	0.011	0.013	0.000	0.013	0.000	0.000	0.000	0.000	0.00	0.52	0.21
Bryce Canyon NP, UT	Warm	0.009	0.000	0.000	0.025	0.018	0.000	0.000	0.000	0.005	0.027	0.000	0.00	0.53	0.00
Canyonlands NP, UT	Cold	0.000	0.000	0.000	0.000	0.010	0.000	0.000	0.000	0.000	0.004	0.000	0.00	0.46	0.17
Canyonlands NP, UT	Warm	0.008	0.000	0.000	0.019	0.021	0.000	0.021	0.000	0.000	0.000	0.000	0.00	0.50	0.00
Cape Romain NWR, SC	Cold	0.016	0.016	0.000	0.035	0.028	0.000	0.034	0.000	0.017	0.074	0.036	0.00	0.68	0.00
Cape Romain NWR, SC	Warm	0.012	0.011	0.006	0.000	0.014	0.000	0.017	0.000	0.000	0.000	0.000	0.00	0.57	0.00
Chassahowitzka NWR, FL	Cold	0.032	0.033	0.015	0.035	0.029	0.000	0.064	0.000	0.017	0.099	0.050	0.00	0.59	0.20
Chassahowitzka NWR, FL	Warm	0.020	0.025	0.012	0.000	0.000	0.000	0.030	0.000	0.000	0.000	0.000	0.00	0.46	0.00
Chilliwack, BC, Canada	Cold	0.051	0.048	0.028	0.100	0.087	0.083	0.144	0.048	0.028	0.273	0.065	0.00	1.05	0.00
Chilliwack, BC, Canada	Warm	0.028	0.033	0.024	0.050	0.048	0.000	0.086	0.000	0.000	0.052	0.000	0.00	1.03	0.36

Table A.1. Ambient Concentrations of Selected Fine Particle Chemical Species - Abbotsford to Chilliwack (all values in ng/m³)

Site	Composite Sample	Levoglucosan	8,15-Pimaradienoic Acid	Pimaric Acid	Sandaracopimaric Acid	Isopimaric Acid	Dehydroabietic Acid	Abietic Acid	Abieta-6,8,11,13,15-pentaen-18-oic Acid	Abieta-6,8,11,13-tetraen-18-oic Acid	Abieta-8,11,13,15-tetraen-18-oic Acid	7-Oxodehydroabietic Acid	Octanoic Acid	Nonanoic Acid	Decanoic Acid
Abbotsford, BC, Canada	Cold	184.2	0.33	0.17	0.27	1.70	7.98	0.49	0.16	1.52	0.73	0.99	0.35	0.49	0.55
Abbotsford, BC, Canada	Warm	64.9	0.07	0.02	0.05	0.29	3.68	0.00	0.06	0.41	0.22	0.53	0.89	1.69	0.97
Acadia NP, ME	Cold	18.9	0.03	0.02	0.02	0.13	1.03	0.00	0.00	0.15	0.04	0.12	0.12	0.52	0.67
Acadia NP, ME	Warm	13.5	0.00	0.00	0.00	0.09	0.17	0.00	0.01	0.02	0.01	0.07	0.16	0.32	0.53
Acadia NP, ME	8/23/95	2547.4	0.00	0.00	0.00	19.68	24.19	0.00	0.37	4.62	6.61	7.17	11.85	19.14	6.06
Badlands NP, SD	Cold	5.4	0.00	0.01	0.01	0.06	0.26	0.00	0.01	0.05	0.02	0.06	0.22	0.67	1.01
Badlands NP, SD	Warm	11.7	0.00	0.00	0.00	0.21	0.20	0.00	0.00	0.03	0.01	0.05	0.19	0.46	0.70
Bandelier NM, NM	Cold	12.8	1.13	0.27	0.12	0.46	3.84	0.05	0.05	0.97	0.30	0.55	0.26	0.84	0.99
Bandelier NM, NM	Warm	8.6	0.41	0.22	0.07	0.33	5.47	0.02	0.04	0.87	0.38	0.75	0.38	0.62	0.85
Big Bend NP, TX	Cold	3.8	0.00	0.00	0.00	0.04	0.15	0.00	0.00	0.02	0.01	0.03	0.25	0.70	0.74
Big Bend NP, TX	Warm	2.7	0.00	0.00	0.00	0.07	0.27	0.00	0.00	0.05	0.01	0.04	0.23	0.49	0.69
Bliss State Park, CA	Cold	44.7	0.17	0.22	0.12	0.72	6.35	0.05	0.07	1.31	0.49	1.26	0.38	1.02	1.33
Bliss State Park, CA	Warm	15.1	0.03	0.03	0.03	0.21	1.63	0.00	0.00	0.41	0.19	0.44	0.15	0.70	0.75
Boundary Waters Canoe Area, MN	Cold	10.8	0.02	0.04	0.02	0.11	0.70	0.00	0.02	0.14	0.05	0.16	0.23	0.60	0.95
Boundary Waters Canoe Area, MN	Warm	21.6	0.00	0.00	0.00	0.00	0.66	0.00	0.00	0.06	0.00	0.14	0.32	0.76	0.86
Boundary Waters Canoe Area, MN	8/12/95	1102.1	3.63	4.76	3.15	19.10	375.41	1.39	2.05	89.56	15.02	25.47	11.70	20.07	5.57
Bridger Wilderness, WY	Cold	3.7	0.01	0.01	0.00	0.03	0.19	0.00	0.00	0.03	0.02	0.05	0.22	0.67	1.05
Bridger Wilderness, WY	Warm	9.7	0.00	0.00	0.00	0.08	0.25	0.00	0.00	0.00	0.00	0.03	0.12	0.42	0.54
Brigantine NWR, NJ	Cold	67.4	0.00	0.05	0.02	0.15	1.01	0.00	0.07	0.15	0.07	0.21	0.19	0.32	0.54
Brigantine NWR, NJ	Warm	10.3	0.00	0.01	0.00	0.12	0.23	0.00	0.05	0.05	0.05	0.13	0.13	0.34	0.44
Brockport, NY	Cold	69.7	0.00	0.00	0.01	0.01	0.41	0.00	0.05	0.06	0.03	0.11	0.44	1.41	0.96
Brockport, NY	Warm	72.7	0.02	0.02	0.00	0.00	0.35	0.00	0.06	0.14	0.08	0.13	0.00	1.01	0.89
Bryce Canyon NP, UT	Cold	0.9	0.03	0.05	0.01	0.07	0.58	0.00	0.01	0.10	0.03	0.08	0.20	0.48	0.85
Bryce Canyon NP, UT	Warm	40.8	2.66	1.89	0.47	2.61	28.24	0.72	0.26	6.84	2.57	2.02	0.30	0.64	1.00
Canyonlands NP, UT	Cold	2.2	0.05	0.01	0.01	0.04	0.25	0.00	0.01	0.06	0.02	0.05	0.21	0.54	0.84
Canyonlands NP, UT	Warm	1.5	0.03	0.01	0.01	0.05	0.20	0.00	0.00	0.03	0.02	0.03	0.23	0.53	0.75
Cape Romain NWR, SC	Cold	70.5	0.05	0.29	0.06	0.17	6.78	0.03	0.09	0.72	0.46	1.53	0.18	0.32	0.43
Cape Romain NWR, SC	Warm	14.1	0.00	0.00	0.00	0.00	1.37	0.00	0.00	0.23	0.11	0.45	0.00	0.23	0.23
Chassahowitzka NWR, FL	Cold	83.0	0.11	0.21	0.07	0.35	8.30	0.00	0.07	0.89	0.47	1.53	0.25	0.35	0.55
Chassahowitzka NWR, FL	Warm	13.5	0.00	0.02	0.01	0.07	0.73	0.00	0.08	0.35	0.24	0.50	0.19	0.17	0.36
Chilliwack, BC, Canada	Cold	157.5	0.04	0.11	0.13	0.77	4.62	0.05	0.11	0.64	0.40	0.80	0.22	0.28	0.46
Chilliwack, BC, Canada	Warm	90.8	0.07	0.02	0.10	0.49	1.77	0.00	0.06	0.22	0.13	0.40	0.46	0.42	0.47

Table A.1. Ambient Concentrations of Selected Fine Particle Chemical Species - Abbotstford to Chilliwack (all values in ng/m³)

Site	Composite Sample	Undecanoic Acid	Dodecanoic Acid	Tridecanoic Acid	Tetradecanoic Acid	Pentadecanoic Acid	Hexadecanoic Acid	Heptadecanoic Acid	Octadecanoic Acid	Nonadecanoic Acid	Eicosanoic Acid	Henicosanoic Acid	Docosanoic Acid	Tricosanoic Acid	Tetracosanoic Acid
Abbotsford, BC, Canada	Cold	0.11	1.35	0.22	2.25	1.23	13.06	0.89	9.15	0.45	2.62	0.74	6.25	1.08	6.30
Abbotsford, BC, Canada	Warm	0.17	2.72	0.24	2.74	1.31	12.45	0.79	8.04	0.27	2.26	0.39	2.98	0.63	3.15
Acadia NP, ME	Cold	0.12	1.46	0.22	1.74	0.79	6.18	0.30	3.91	0.12	0.58	0.00	1.24	0.29	1.19
Acadia NP, ME	Warm	0.09	1.09	0.18	1.71	0.97	8.98	0.46	4.28	0.15	0.93	0.20	1.16	0.34	1.17
Acadia NP, ME	8/23/95	1.55	15.17	2.47	17.50	9.90	64.28	12.29	80.79	30.07	225.38	42.69	263.07	52.95	177.50
Badlands NP, SD	Cold	0.16	1.65	0.29	2.67	0.98	6.29	0.31	3.42	0.08	0.40	0.13	0.83	0.23	0.84
Badlands NP, SD	Warm	0.13	1.27	0.29	2.73	0.76	7.97	0.51	4.95	0.27	2.12	0.44	2.61	0.73	2.55
Bandelier NM, NM	Cold	0.17	2.13	0.29	2.15	0.93	5.81	0.34	4.29	0.10	0.83	0.19	1.67	0.38	1.68
Bandelier NM, NM	Warm	0.15	1.77	0.29	2.35	1.03	7.37	0.44	4.40	0.15	0.99	0.21	2.14	0.43	2.03
Big Bend NP, TX	Cold	0.13	1.48	0.20	1.60	0.74	4.74	0.30	3.51	0.08	0.43	0.16	0.77	0.37	1.22
Big Bend NP, TX	Warm	0.14	1.43	0.25	1.75	0.78	6.74	0.44	5.17	0.13	0.65	0.22	1.18	0.51	1.75
Bliss State Park, CA	Cold	0.27	2.48	0.47	2.46	1.17	6.14	0.46	3.42	0.36	2.28	0.54	6.84	1.00	5.42
Bliss State Park, CA	Warm	0.20	1.99	0.38	2.61	1.27	8.65	0.57	4.57	0.27	1.25	0.00	4.02	0.58	3.07
Boundary Waters Canoe Area, MN	Cold	0.17	1.65	0.27	1.88	0.87	5.73	0.34	3.67	0.14	0.71	0.26	1.45	0.35	1.49
Boundary Waters Canoe Area, MN	Warm	0.17	2.37	0.36	2.99	1.22	8.67	0.51	4.95	0.50	4.45	0.88	5.25	1.45	4.02
Boundary Waters Canoe Area, MN	8/12/95	0.93	9.72	1.59	9.99	5.81	49.09	4.33	48.27	11.81	102.00	20.75	184.55	39.35	155.18
Bridger Wilderness, WY	Cold	0.19	1.89	0.26	1.72	0.63	4.29	0.24	3.05	0.05	0.23	0.06	0.45	0.12	0.47
Bridger Wilderness, WY	Warm	0.11	1.37	0.20	2.02	0.71	6.68	0.32	3.63	0.15	0.82	0.00	2.12	0.29	1.02
Brigantine NWR, NJ	Cold	0.11	1.37	0.24	1.82	0.85	7.79	0.48	5.16	0.22	0.86	0.57	2.46	0.91	4.03
Brigantine NWR, NJ	Warm	0.07	0.99	0.18	1.48	0.71	7.13	0.45	4.54	0.18	1.29	0.32	1.80	0.58	1.95
Brockport, NY	Cold	0.33	2.42	0.38	1.53	1.00	9.47	0.55	4.58	0.23	0.91	0.49	2.43	0.74	2.78
Brockport, NY	Warm	0.32	4.29	0.70	3.44	1.30	14.65	0.70	5.87	0.28	1.77	0.37	2.40	0.67	2.33
Bryce Canyon NP, UT	Cold	0.17	2.07	0.32	2.00	0.90	4.64	0.25	3.13	0.04	0.19	0.05	0.36	0.10	0.38
Bryce Canyon NP, UT	Warm	0.19	2.42	0.40	2.81	1.22	7.59	0.45	3.78	0.18	1.37	0.28	3.18	0.50	2.30
Canyonlands NP, UT	Cold	0.14	1.58	0.26	1.72	0.69	4.62	0.25	3.39	0.05	0.25	0.08	0.50	0.14	0.53
Canyonlands NP, UT	Warm	0.13	1.45	0.24	1.92	0.81	7.20	0.38	3.96	0.10	0.42	0.16	0.99	0.28	1.09
Cape Romain NWR, SC	Cold	0.10	1.11	0.21	1.54	0.79	7.41	0.42	4.67	0.17	0.86	0.47	2.30	1.11	4.59
Cape Romain NWR, SC	Warm	0.00	1.02	0.00	1.72	0.94	10.39	0.40	5.95	0.00	0.61	0.00	0.68	0.27	1.13
Chassahowitzka NWR, FL	Cold	0.11	1.38	0.22	1.56	0.78	7.96	0.52	6.02	0.25	1.03	0.62	2.78	1.50	8.74
Chassahowitzka NWR, FL	Warm	0.04	0.89	0.15	1.21	0.57	6.33	0.35	5.23	0.11	0.54	0.17	0.90	0.43	2.19
Chilliwack, BC, Canada	Cold	0.08	1.56	0.31	2.28	1.04	10.50	0.68	7.31	0.37	2.28	0.68	5.29	1.04	5.34
Chilliwack, BC, Canada	Warm	0.11	1.15	0.29	2.17	1.05	11.90	0.59	6.14	0.21	1.20	0.36	2.49	0.60	2.83

Table A.1. Ambient Concentrations of Selected Fine Particle Chemical Species - Abbotsford to Chilliwack (all values in ng/m³)

Site	Composite Sample	Pentacosanoic Acid	Hexacosanoic Acid	Heptacosanoic Acid	Octacosanoic Acid	Nonacosanoic Acid	Triacontanoic Acid	Hentriacontanoic Acid	Dotriacontanoic Acid	9-Hexadecenoic Acid	9,12-Octadecanedienoic Acid	9-Octadecenoic Acid	Propanedioic Acid	Methylpropanedioic Acid	Butanedioic Acid
Abbotsford, BC, Canada	Cold	0.60	1.85	0.17	0.62	0.10	0.49	0.04	0.17	2.23	0.68	1.81	0.72	0.00	7.72
Abbotsford, BC, Canada	Warm	0.42	1.14	0.12	0.45	0.00	0.30	0.00	0.00	2.35	1.15	2.33	0.00	0.00	4.96
Acadia NP, ME	Cold	0.13	0.53	0.03	0.13	0.00	0.04	0.00	0.00	1.78	0.24	1.28	1.31	0.00	4.88
Acadia NP, ME	Warm	0.23	0.66	0.11	0.52	0.06	0.27	0.02	0.08	1.48	0.49	1.37	10.25	0.60	16.09
Acadia NP, ME	8/23/95	21.56	43.18	9.59	31.40	4.58	15.10	1.27	4.13	21.63	3.52	21.12	0.00	0.00	13.22
Badlands NP, SD	Cold	0.15	0.45	0.07	0.35	0.05	0.32	0.00	0.09	2.50	0.31	1.78	0.63	0.00	4.37
Badlands NP, SD	Warm	0.50	1.74	0.40	2.66	0.32	2.81	0.13	1.00	1.91	0.68	1.54	1.69	0.29	8.74
Bandelier NM, NM	Cold	0.19	0.60	0.09	0.37	0.04	0.29	0.02	0.10	2.07	0.24	1.38	0.33	0.00	4.17
Bandelier NM, NM	Warm	0.23	0.64	0.11	0.71	0.09	0.62	0.03	0.19	2.32	0.63	1.73	1.70	0.00	7.16
Big Bend NP, TX	Cold	0.27	0.87	0.20	1.08	0.18	1.14	0.09	0.48	1.67	0.29	1.33	1.29	0.00	6.74
Big Bend NP, TX	Warm	0.38	1.13	0.28	1.35	0.23	1.29	0.09	0.44	1.56	0.22	1.18	3.69	0.38	10.63
Bliss State Park, CA	Cold	0.40	0.91	0.10	0.40	0.08	0.34	0.02	0.10	1.82	0.30	1.71	0.29	0.00	5.87
Bliss State Park, CA	Warm	0.22	0.59	0.09	0.32	0.00	0.19	0.00	0.00	1.83	0.27	1.43	2.80	0.00	9.29
Boundary Waters Canoe Area, MN	Cold	0.20	0.71	0.09	0.39	0.04	0.18	0.00	0.07	2.00	0.29	1.57	0.77	0.00	6.25
Boundary Waters Canoe Area, MN	Warm	0.73	2.18	0.37	1.84	0.20	0.79	0.06	0.27	2.41	1.40	2.07	2.10	0.00	11.03
Boundary Waters Canoe Area, MN	8/12/95	14.46	47.67	6.03	27.74	1.97	7.26	0.67	3.03	5.95	2.87	11.71	0.00	0.00	6.21
Bridger Wilderness, WY	Cold	0.07	0.17	0.03	0.09	0.01	0.07	0.00	0.01	1.57	0.24	1.32	0.14	0.00	1.78
Bridger Wilderness, WY	Warm	0.08	0.47	0.00	0.31	0.00	0.15	0.00	0.00	1.56	0.41	1.40	0.00	0.00	4.25
Brigantine NWR, NJ	Cold	0.50	2.06	0.13	0.62	0.08	0.38	0.02	0.16	1.68	0.36	1.39	1.61	0.00	9.74
Brigantine NWR, NJ	Warm	0.35	1.20	0.20	1.05	0.14	0.73	0.05	0.22	1.73	0.57	1.50	14.90	0.75	21.47
Brockport, NY	Cold	0.38	1.28	0.14	0.64	0.09	0.38	0.02	0.11	0.40	0.26	1.10	4.83	0.00	16.42
Brockport, NY	Warm	0.36	1.32	0.20	1.19	0.12	0.68	0.03	0.16	0.91	0.28	0.92	5.55	0.00	23.33
Bryce Canyon NP, UT	Cold	0.06	0.15	0.02	0.10	0.01	0.06	0.00	0.02	1.63	0.29	1.39	0.29	0.00	2.42
Bryce Canyon NP, UT	Warm	0.22	0.61	0.11	0.51	0.07	0.43	0.02	0.11	2.09	0.33	1.61	0.83	0.00	5.36
Canyonlands NP, UT	Cold	0.09	0.23	0.04	0.15	0.02	0.09	0.00	0.03	1.24	0.16	1.06	0.19	0.00	2.01
Canyonlands NP, UT	Warm	0.17	0.47	0.10	0.45	0.07	0.34	0.02	0.08	1.64	0.17	1.36	0.54	0.00	3.65
Cape Romain NWR, SC	Cold	0.54	2.77	0.24	1.10	0.22	1.01	0.13	0.47	1.52	1.51	1.30	2.94	0.28	12.32
Cape Romain NWR, SC	Warm	0.00	0.58	0.00	0.30	0.00	0.00	0.00	0.00	1.92	4.43	3.84	10.97	0.00	10.37
Chassahowitzka NWR, FL	Cold	0.81	5.22	0.26	1.13	0.21	0.86	0.11	0.40	1.53	1.06	1.50	2.99	0.20	10.00
Chassahowitzka NWR, FL	Warm	0.31	1.45	0.17	0.72	0.14	0.59	0.07	0.25	1.33	2.22	2.14	4.79	0.41	9.31
Chilliwack, BC, Canada	Cold	0.46	1.49	0.10	0.53	0.06	0.36	0.00	0.08	2.01	0.40	1.46	0.00	0.00	4.86
Chilliwack, BC, Canada	Warm	0.31	1.11	0.12	0.57	0.06	0.31	0.00	0.07	2.53	0.51	2.24	1.08	0.00	9.83

Table A.1. Ambient Concentrations of Selected Fine Particle Chemical Species - Abbotstford to Chilliwack (all values in ng/m³)

Site	Composite Sample	Methylbutanedioic Acid	Pentanedioic Acid	Hexanedioic Acid	Heptanedioic Acid	Octanedioic Acid	Nonanedioic Acid
Abbotsford, BC, Canada	Cold	2.11	2.06	1.71	1.48	1.46	5.64
Abbotsford, BC, Canada	Warm	0.87	1.35	1.44	0.41	0.98	3.10
Acadia NP, ME	Cold	0.00	1.68	5.00	1.20	0.89	2.64
Acadia NP, ME	Warm	1.09	3.94	4.56	1.38	1.60	3.19
Acadia NP, ME	8/23/95	3.56	4.72	5.61	6.53	21.84	45.14
Badlands NP, SD	Cold	0.74	1.43	1.51	0.51	0.63	1.11
Badlands NP, SD	Warm	0.92	2.25	1.91	0.95	1.57	2.36
Bandelier NM, NM	Cold	0.76	1.42	1.52	0.39	0.88	2.90
Bandelier NM, NM	Warm	0.75	1.88	1.69	0.68	1.33	3.16
Big Bend NP, TX	Cold	0.76	1.67	1.67	0.79	0.73	1.31
Big Bend NP, TX	Warm	0.83	1.94	2.24	0.68	0.94	1.65
Bliss State Park, CA	Cold	1.28	1.97	2.13	0.79	1.80	4.13
Bliss State Park, CA	Warm	2.35	2.94	2.11	1.02	1.87	2.55
Boundary Waters Canoe Area, MN	Cold	0.97	2.08	3.93	0.83	0.73	1.90
Boundary Waters Canoe Area, MN	Warm	1.16	2.72	2.26	1.14	1.98	3.48
Boundary Waters Canoe Area, MN	8/12/95	1.82	2.32	3.00	1.52	5.27	24.05
Bridger Wilderness, WY	Cold	0.28	0.60	1.61	0.18	0.59	0.98
Bridger Wilderness, WY	Warm	0.00	1.41	1.36	0.58	0.93	1.45
Brigantine NWR, NJ	Cold	1.61	2.85	2.13	2.39	1.20	3.86
Brigantine NWR, NJ	Warm	1.24	4.31	3.40	2.21	1.39	3.73
Brockport, NY	Cold	3.28	8.23	4.18	2.40	1.30	4.40
Brockport, NY	Warm	2.11	6.85	4.59	1.58	2.70	8.83
Bryce Canyon NP, UT	Cold	0.35	0.77	1.38	0.21	0.48	0.87
Bryce Canyon NP, UT	Warm	0.84	1.57	1.35	0.57	1.21	2.64
Canyonlands NP, UT	Cold	0.31	0.71	1.02	0.22	0.59	2.04
Canyonlands NP, UT	Warm	0.39	1.12	1.17	0.47	1.03	3.30
Cape Romain NWR, SC	Cold	1.79	3.10	2.84	1.20	2.40	4.93
Cape Romain NWR, SC	Warm	0.00	1.41	4.75	0.00	0.00	3.00
Chassahowitzka NWR, FL	Cold	1.48	2.52	2.51	1.01	1.90	5.35
Chassahowitzka NWR, FL	Warm	0.70	1.75	4.51	0.86	1.41	5.54
Chilliwack, BC, Canada	Cold	1.70	1.70	1.92	1.43	1.34	4.85
Chilliwack, BC, Canada	Warm	1.27	2.67	1.89	1.80	1.63	3.84

Table A.2. Ambient Concentrations of Selected Fine Particle Chemical Species - Chiricahua to Jefferson/James (all values in ng/m³)

Site	Composite Sample	Total Carbon	Silicon	Aluminum	Potassium	Guaiacyl Acetone	Acetovanillone	Vanillin	Syringaldehyde	Homovanillic Acid	Vanillic Acid	Sinapyl Aldehyde	Syringic Acid	Syringyl Acetone	Propionyl Syringol
Chiricahua NM, AZ	Cold	535	120	45	13	0.00	0.00	0.05	0.08	0.00	0.00	0.00	0.00	0.00	0.00
Chiricahua NM, AZ	Warm	880	248	88	27	0.00	0.00	0.03	0.05	0.00	0.00	0.00	0.00	0.00	0.00
Columbia River Gorge, WA	Cold	2256	51	80	18	0.00	0.00	0.36	0.12	0.00	0.00	0.00	0.00	0.00	0.07
Columbia River Gorge, WA	Warm	1909	144	65	25	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Crater Lake NP, OR	Cold	685	49	18	7	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Crater Lake NP, OR	Warm	1095	94	40	11	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Denali NP, AK	Cold	231	36	16	5	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Denali NP, AK	Warm	378	44	19	5	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dolly Sods Wilderness, WV	Cold	1976	67	31	22	0.18	0.12	0.30	6.01	0.89	2.81	0.00	22.79	1.22	5.65
Dolly Sods Wilderness, WV	Warm	2381	146	55	26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.52	0.00	0.68
Gila Wilderness, NM	Cold	904	76	36	9	0.14	0.06	0.32	0.24	0.00	1.17	0.00	0.00	0.07	0.04
Gila Wilderness, NM	Warm	1442	191	67	24	0.40	0.14	0.56	0.17	0.00	3.39	0.00	0.00	0.15	0.05
Glacier NP, MT	Cold	1796	43	35	11	0.26	0.09	0.73	0.09	0.00	2.56	0.00	0.00	0.03	0.04
Glacier NP, MT	Warm	2009	135	60	13	0.18	0.05	0.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Grand Canyon NP, AZ	Cold	467	76	34	7	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00
Grand Canyon NP, AZ	Warm	842	154	57	20	0.00	0.00	0.06	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Great Basin NP, NV	Cold	590	78	31	8	0.05	0.04	0.11	0.18	0.00	0.00	0.00	0.00	0.00	0.05
Great Basin NP, NV	Warm	752	149	52	18	0.00	0.00	0.04	0.12	0.00	0.00	0.00	0.00	0.00	0.02
Great Gulf Wilderness, NH	Warm	2326	68	21	33	0.09	0.00	0.16	0.13	0.00	0.00	0.00	1.58	0.09	0.07
Great Sand Dunes NM, CO	Cold	540	158	55	9	0.00	0.00	0.11	1.54	0.00	0.00	0.00	0.00	0.00	0.23
Great Sand Dunes NM, CO	Warm	783	250	75	17	0.00	0.00	0.07	0.07	0.00	0.00	0.00	0.00	0.00	0.00
Great Smoky Mountains NP, TN	Cold	1860	65	25	31	0.09	0.05	0.28	0.50	0.00	0.00	0.00	1.74	0.17	0.13
Great Smoky Mountains NP, TN	Warm	2888	199	86	32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Guadalupe Mountains NP, TX	Cold	734	180	83	17	0.00	0.00	0.13	0.05	0.00	0.00	0.00	0.00	0.00	0.00
Guadalupe Mountains NP, TX	Warm	863	304	119	19	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Indian Gardens, AZ	Cold	790	108	45	9	0.05	0.03	0.10	0.59	0.00	0.00	0.00	0.00	0.05	0.27
Indian Gardens, AZ	Warm	1136	245	87	29	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Jarbridge Wilderness, NV	Cold	416	59	23	7	0.00	0.00	0.12	0.25	0.00	0.00	0.00	0.00	0.00	0.00
Jarbridge Wilderness, NV	Warm	1002	264	89	23	0.06	0.04	0.18	0.65	0.00	0.00	0.00	1.81	0.17	0.17
Jefferson/James River Face, VA	Cold	3808	104	55	62	1.02	0.28	1.81	4.15	3.58	5.06	0.00	34.23	4.19	6.87
Jefferson/James River Face, VA	Warm	3586	122	45	41	0.32	0.08	0.00	0.00	0.00	0.00	0.00	10.68	0.30	0.33

Table A.2. Ambient Concentrations of Selected Fine Particle Chemical Species - Chiricahua to Jefferson/James (all values in ng/m³)

Site	Composite Sample	Acetosyringone	Acetonylsyringol	Juvabione	Dehydrojuvabione	Beta-Sitosterol	Stigmast-4-en-3-one	Stigmasta-3,5-dien-7-one	Stigmasta-4,6-dien-3-one	Stigmastan-3-ol	Stigmastan-3-one	Friedelin	Beta-Amyrone	Beta-Amyrin	Alpha-Amyrone
Chiricahua NM, AZ	Cold	0.04	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Chiricahua NM, AZ	Warm	0.02	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.02	0.00	0.00	0.01
Columbia River Gorge, WA	Cold	0.17	0.05	0.00	0.00	0.34	0.18	0.06	0.03	0.16	0.05	0.26	0.01	0.01	0.01
Columbia River Gorge, WA	Warm	0.00	0.00	0.00	0.00	0.14	0.09	0.02	0.01	0.07	0.02	0.05	0.00	0.00	0.00
Crater Lake NP, OR	Cold	0.03	0.00	0.00	0.00	0.00	0.03	0.01	0.00	0.00	0.01	0.05	0.00	0.00	0.00
Crater Lake NP, OR	Warm	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.01
Denali NP, AK	Cold	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Denali NP, AK	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dolly Sods Wilderness, WV	Cold	16.21	1.47	0.00	0.00	0.73	0.31	0.09	0.04	0.31	0.09	0.21	0.01	0.01	0.01
Dolly Sods Wilderness, WV	Warm	1.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gila Wilderness, NM	Cold	0.12	0.09	0.00	0.00	0.41	0.30	0.12	0.05	0.07	0.07	0.12	0.01	0.01	0.01
Gila Wilderness, NM	Warm	0.11	0.17	0.00	0.00	0.59	0.75	0.37	0.12	0.14	0.10	0.41	0.02	0.02	0.04
Glacier NP, MT	Cold	0.09	0.05	0.05	0.00	0.45	0.25	0.15	0.05	0.13	0.05	0.00	0.00	0.00	0.01
Glacier NP, MT	Warm	0.00	0.05	0.00	0.00	0.25	0.27	0.10	0.03	0.08	0.06	0.00	0.00	0.00	0.01
Grand Canyon NP, AZ	Cold	0.04	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Grand Canyon NP, AZ	Warm	0.01	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Great Basin NP, NV	Cold	0.19	0.00	0.00	0.00	0.12	0.04	0.03	0.01	0.00	0.01	0.00	0.00	0.00	0.00
Great Basin NP, NV	Warm	0.09	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Great Gulf Wilderness, NH	Warm	0.13	0.13	0.00	0.00	0.17	0.18	0.08	0.04	0.11	0.04	0.21	0.02	0.02	0.05
Great Sand Dunes NM, CO	Cold	0.62	0.08	0.00	0.00	0.22	0.10	0.05	0.02	0.04	0.02	0.00	0.01	0.01	0.03
Great Sand Dunes NM, CO	Warm	0.06	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Great Smoky Mountains NP, TN	Cold	0.30	0.23	0.00	0.00	0.24	0.18	0.05	0.03	0.06	0.05	0.42	0.01	0.03	0.02
Great Smoky Mountains NP, TN	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Guadalupe Mountains NP, TX	Cold	0.05	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Guadalupe Mountains NP, TX	Warm	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Indian Gardens, AZ	Cold	0.56	0.08	0.00	0.00	0.23	0.09	0.06	0.02	0.05	0.03	0.00	0.01	0.01	0.04
Indian Gardens, AZ	Warm	0.00	0.04	0.00	0.00	0.07	0.05	0.02	0.00	0.00	0.01	0.00	0.00	0.00	0.01
Jarbridge Wilderness, NV	Cold	0.13	0.00	0.00	0.00	0.06	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Jarbridge Wilderness, NV	Warm	0.42	0.21	0.00	0.00	0.22	0.16	0.10	0.02	0.09	0.05	0.00	0.05	0.03	0.10
Jefferson/James River Face, VA	Cold	14.17	4.87	0.00	0.00	2.16	0.99	0.44	0.21	0.54	0.10	1.77	0.06	0.13	0.11
Jefferson/James River Face, VA	Warm	0.65	0.31	0.00	0.00	0.00	2.13	1.14	0.42	0.00	0.27	5.98	0.20	0.00	0.58

Table A.2. Ambient Concentrations of Selected Fine Particle Chemical Species - Chiricahua to Jefferson/James (all values in ng/m³)

Site	Composite Sample	Alpha-Amyrin	Alpha-Tocopherol	Delta-Tocopherol	Beta-Tocopherol	Betulin	Cholesterol	Hexadecane	Heptadecane	Octadecane	Nonadecane	Eicosane	Heneicosane	Docosane	Tricosane
Chiricahua NM, AZ	Cold	0.00	0.00	0.00	0.00	0.00	0.17	5.49	0.00	0.00	0.06	0.08	0.13	0.17	0.26
Chiricahua NM, AZ	Warm	0.01	0.00	0.00	0.00	0.00	0.23	0.00	0.00	0.00	0.04	0.07	0.10	0.14	0.23
Columbia River Gorge, WA	Cold	0.01	0.00	0.00	0.00	0.00	0.39	0.00	0.03	0.00	0.05	0.08	0.16	0.29	0.54
Columbia River Gorge, WA	Warm	0.01	0.00	0.00	0.00	0.00	0.16	0.00	0.01	0.00	0.05	0.08	0.10	0.18	0.37
Crater Lake NP, OR	Cold	0.00	0.00	0.00	0.00	0.00	0.18	10.84	0.01	0.00	0.07	0.11	0.23	0.42	0.65
Crater Lake NP, OR	Warm	0.00	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.00	0.07	0.11	0.17	0.34
Denali NP, AK	Cold	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.03	0.00	0.00	0.11	0.21	0.26	0.32
Denali NP, AK	Warm	0.00	0.00	0.00	0.00	0.00	0.19	0.00	0.00	0.00	0.00	0.07	0.15	0.18	0.39
Dolly Sods Wilderness, WV	Cold	0.02	0.00	0.00	0.00	0.00	0.24	0.00	0.00	0.00	0.00	0.10	0.17	0.29	0.50
Dolly Sods Wilderness, WV	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.11	0.21	0.52
Gila Wilderness, NM	Cold	0.01	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.08	0.00	0.10	0.13	0.18	0.27
Gila Wilderness, NM	Warm	0.04	0.06	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00	0.07	0.11	0.15	0.32
Glacier NP, MT	Cold	0.01	0.00	0.00	0.00	0.00	0.23	0.00	0.00	0.00	0.00	0.10	0.21	0.48	0.80
Glacier NP, MT	Warm	0.02	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.00	0.08	0.08	0.15	0.36
Grand Canyon NP, AZ	Cold	0.00	0.00	0.00	0.00	0.00	0.14	0.00	0.00	0.00	0.00	0.08	0.15	0.18	0.29
Grand Canyon NP, AZ	Warm	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.10	0.17	0.22	0.49
Great Basin NP, NV	Cold	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.09	0.16	0.22	0.28
Great Basin NP, NV	Warm	0.00	0.00	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.00	0.09	0.16	0.23	0.51
Great Gulf Wilderness, NH	Warm	0.03	0.00	0.00	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.08	0.09	0.17	0.68
Great Sand Dunes NM, CO	Cold	0.04	0.00	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.00	0.11	0.18	0.22	0.35
Great Sand Dunes NM, CO	Warm	0.01	0.00	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.06	0.12	0.14	0.31
Great Smoky Mountains NP, TN	Cold	0.04	0.00	0.00	0.00	0.00	0.34	0.00	0.00	0.00	0.00	0.06	0.13	0.22	0.50
Great Smoky Mountains NP, TN	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.12	0.32
Guadalupe Mountains NP, TX	Cold	0.00	0.00	0.00	0.00	0.00	0.33	0.00	0.00	0.00	0.00	0.15	0.27	0.34	0.48
Guadalupe Mountains NP, TX	Warm	0.00	0.00	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.00	0.08	0.12	0.15	0.25
Indian Gardens, AZ	Cold	0.05	0.00	0.00	0.00	0.00	0.34	0.00	0.00	0.00	0.00	0.11	0.19	0.25	0.49
Indian Gardens, AZ	Warm	0.01	0.00	0.00	0.00	0.00	0.22	0.01	0.00	0.00	0.00	0.12	0.11	0.15	0.39
Jarbridge Wilderness, NV	Cold	0.01	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.00	0.08	0.15	0.19	0.25
Jarbridge Wilderness, NV	Warm	0.07	0.00	0.00	0.00	0.00	0.20	0.00	0.00	0.00	0.00	0.09	0.15	0.18	0.43
Jefferson/James River Face, VA	Cold	0.17	0.27	0.00	0.00	0.00	0.20	0.00	0.00	0.00	0.00	0.13	0.23	0.48	1.08
Jefferson/James River Face, VA	Warm	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.00	0.11	0.26

Table A.2. Ambient Concentrations of Selected Fine Particle Chemical Species - Chiricahua to Jefferson/James (all values in ng/m³)

Site	Composite Sample	Tetracosane	Pentacosane	Hexacosane	Heptacosane	Octacosane	Nonacosane	Triacosane	Hentriacontane	Dotriacontane	Tritriacontane	Tetratriacontane	Pentatriacontane	Hexatriacontane	Fluoranthene
Chiricahua NM, AZ	Cold	0.30	0.34	0.24	0.28	0.14	0.40	0.10	0.27	0.07	0.10	0.00	0.00	0.00	0.004
Chiricahua NM, AZ	Warm	0.32	0.55	0.35	0.60	0.27	1.07	0.14	0.46	0.09	0.17	0.08	0.00	0.00	0.003
Columbia River Gorge, WA	Cold	0.79	1.03	0.63	0.63	0.41	0.73	0.27	0.53	0.15	0.17	0.00	0.00	0.00	0.298
Columbia River Gorge, WA	Warm	0.51	1.08	0.40	0.78	0.31	1.27	0.24	0.97	0.00	0.16	0.00	0.00	0.00	0.051
Crater Lake NP, OR	Cold	0.89	0.68	0.40	0.30	0.19	0.22	0.11	0.17	0.06	0.06	0.00	0.00	0.00	0.014
Crater Lake NP, OR	Warm	0.61	0.79	0.43	0.49	0.24	0.54	0.15	0.42	0.10	0.16	0.07	0.00	0.00	0.004
Denali NP, AK	Cold	0.38	0.38	0.25	0.33	0.15	0.23	0.11	0.16	0.06	0.04	0.00	0.00	0.00	0.014
Denali NP, AK	Warm	0.42	0.65	0.32	0.40	0.13	0.18	0.09	0.12	0.05	0.00	0.00	0.00	0.00	0.002
Dolly Sods Wilderness, WV	Cold	0.64	0.78	0.53	0.65	0.32	0.65	0.27	0.51	0.16	0.18	0.00	0.00	0.00	0.055
Dolly Sods Wilderness, WV	Warm	0.54	1.03	0.59	1.01	0.43	1.10	0.32	0.83	0.15	0.30	0.00	0.00	0.00	0.027
Gila Wilderness, NM	Cold	0.36	0.43	0.31	0.31	0.22	0.41	0.18	0.28	0.09	0.17	0.00	0.00	0.00	0.006
Gila Wilderness, NM	Warm	0.44	0.78	0.70	1.16	0.72	1.57	0.62	0.97	0.45	0.47	0.30	0.22	0.00	0.006
Glacier NP, MT	Cold	0.93	1.10	0.71	0.65	0.31	0.41	0.18	0.23	0.00	0.00	0.00	0.00	0.00	0.188
Glacier NP, MT	Warm	0.40	0.88	0.51	0.85	0.30	0.96	0.17	0.70	0.10	0.16	0.00	0.00	0.00	0.065
Grand Canyon NP, AZ	Cold	0.27	0.28	0.17	0.20	0.12	0.23	0.08	0.15	0.05	0.04	0.00	0.00	0.00	0.005
Grand Canyon NP, AZ	Warm	0.52	0.61	0.41	0.57	0.32	0.73	0.17	0.39	0.10	0.13	0.07	0.00	0.00	0.004
Great Basin NP, NV	Cold	0.27	0.29	0.16	0.17	0.10	0.21	0.08	0.13	0.00	0.00	0.00	0.00	0.00	0.010
Great Basin NP, NV	Warm	0.62	0.68	0.35	0.42	0.19	0.75	0.13	0.40	0.07	0.11	0.00	0.00	0.00	0.003
Great Gulf Wilderness, NH	Warm	0.72	1.42	0.66	1.40	0.39	1.05	0.29	0.89	0.19	0.27	0.00	0.00	0.00	0.013
Great Sand Dunes NM, CO	Cold	0.27	0.34	0.17	0.23	0.11	0.27	0.08	0.21	0.05	0.07	0.00	0.00	0.00	0.008
Great Sand Dunes NM, CO	Warm	0.33	0.50	0.26	0.44	0.17	0.80	0.12	0.58	0.08	0.16	0.04	0.04	0.00	0.005
Great Smoky Mountains NP, TN	Cold	0.70	0.88	0.48	0.71	0.33	0.87	0.26	0.68	0.16	0.27	0.00	0.00	0.00	0.041
Great Smoky Mountains NP, TN	Warm	0.32	0.58	0.26	0.64	0.31	0.94	0.23	0.71	0.14	0.26	0.08	0.09	0.00	0.013
Guadalupe Mountains NP, TX	Cold	0.50	0.51	0.32	0.53	0.27	1.01	0.23	0.94	0.14	0.43	0.09	0.10	0.00	0.013
Guadalupe Mountains NP, TX	Warm	0.34	0.41	0.24	0.53	0.30	1.24	0.21	0.80	0.16	0.32	0.10	0.10	0.00	0.005
Indian Gardens, AZ	Cold	0.41	0.45	0.33	0.35	0.22	0.63	0.17	0.39	0.10	0.14	0.06	0.00	0.00	0.010
Indian Gardens, AZ	Warm	0.46	0.95	0.55	1.04	0.67	1.84	0.50	1.19	0.42	0.45	0.26	0.19	0.11	0.006
Jarbridge Wilderness, NV	Cold	0.32	0.29	0.19	0.21	0.13	0.25	0.11	0.19	0.07	0.00	0.00	0.00	0.00	0.005
Jarbridge Wilderness, NV	Warm	0.35	0.80	0.43	0.76	0.28	1.21	0.21	0.75	0.11	0.18	0.00	0.00	0.00	0.004
Jefferson/James River Face, VA	Cold	1.05	1.52	0.82	1.41	0.47	1.00	0.37	0.70	0.21	0.25	0.17	0.00	0.00	0.106
Jefferson/James River Face, VA	Warm	0.34	0.63	0.44	0.85	0.41	1.10	0.30	0.83	0.19	0.26	0.08	0.00	0.00	0.028

Table A.2. Ambient Concentrations of Selected Fine Particle Chemical Species - Chiricahua to Jefferson/James (all values in ng/m³)

Site	Composite Sample	Acphenanthrylene	Pyrene	Retene	Benzo(ghi)fluoranthene	Cyclopenta(cd)pyrene	Benz(a)anthracene	Chrysene/triphenylene	Benzo(k)fluoranthene	Benzo(b)fluoranthene	Benzo(i)fluoranthene	Benzo(e)pyrene	Benzo(a)pyrene	Perylene	Indeno(cd)pyrene
Chiricahua NM, AZ	Cold	0.000	0.005	0.020	0.003	0.001	0.002	0.004	0.006	0.009	0.000	0.011	0.005	0.000	0.004
Chiricahua NM, AZ	Warm	0.000	0.004	0.031	0.003	0.000	0.001	0.004	0.005	0.005	0.000	0.010	0.000	0.000	0.003
Columbia River Gorge, WA	Cold	0.011	0.328	0.104	0.078	0.030	0.163	1.043	1.101	3.084	0.016	1.849	0.441	0.051	0.684
Columbia River Gorge, WA	Warm	0.001	0.052	0.024	0.015	0.004	0.016	0.155	0.164	0.452	0.007	0.291	0.065	0.012	0.126
Crater Lake NP, OR	Cold	0.001	0.025	0.050	0.012	0.001	0.005	0.012	0.025	0.021	0.000	0.027	0.011	0.000	0.022
Crater Lake NP, OR	Warm	0.000	0.007	0.024	0.006	0.000	0.001	0.004	0.009	0.009	0.000	0.015	0.004	0.000	0.009
Denali NP, AK	Cold	0.002	0.016	0.025	0.008	0.001	0.004	0.010	0.016	0.016	0.000	0.015	0.006	0.000	0.008
Denali NP, AK	Warm	0.000	0.007	0.012	0.004	0.000	0.001	0.003	0.007	0.007	0.000	0.011	0.003	0.000	0.005
Dolly Sods Wilderness, WV	Cold	0.008	0.054	0.038	0.046	0.014	0.053	0.135	0.161	0.208	0.014	0.155	0.096	0.013	0.135
Dolly Sods Wilderness, WV	Warm	0.001	0.025	0.011	0.015	0.002	0.009	0.030	0.047	0.060	0.005	0.045	0.014	0.000	0.037
Gila Wilderness, NM	Cold	0.002	0.008	0.375	0.006	0.003	0.005	0.012	0.020	0.020	0.003	0.017	0.009	0.004	0.016
Gila Wilderness, NM	Warm	0.005	0.010	0.310	0.010	0.005	0.004	0.012	0.018	0.018	0.000	0.024	0.010	0.004	0.024
Glacier NP, MT	Cold	0.011	0.189	0.206	0.071	0.036	0.199	0.843	0.508	1.117	0.013	0.679	0.255	0.034	0.328
Glacier NP, MT	Warm	0.005	0.062	0.091	0.016	0.006	0.033	0.226	0.207	0.475	0.000	0.326	0.081	0.007	0.141
Grand Canyon NP, AZ	Cold	0.000	0.006	0.027	0.005	0.000	0.002	0.004	0.005	0.007	0.000	0.007	0.000	0.000	0.003
Grand Canyon NP, AZ	Warm	0.000	0.008	0.034	0.006	0.000	0.000	0.004	0.005	0.006	0.000	0.009	0.004	0.000	0.004
Great Basin NP, NV	Cold	0.002	0.013	0.111	0.012	0.002	0.008	0.016	0.030	0.028	0.000	0.023	0.013	0.005	0.018
Great Basin NP, NV	Warm	0.000	0.006	0.028	0.004	0.000	0.000	0.004	0.005	0.007	0.000	0.011	0.005	0.000	0.005
Great Gulf Wilderness, NH	Warm	0.002	0.014	0.017	0.009	0.002	0.004	0.017	0.019	0.045	0.000	0.036	0.007	0.000	0.025
Great Sand Dunes NM, CO	Cold	0.002	0.009	0.047	0.007	0.001	0.004	0.012	0.021	0.022	0.000	0.019	0.007	0.000	0.013
Great Sand Dunes NM, CO	Warm	0.000	0.006	0.025	0.005	0.000	0.001	0.004	0.005	0.006	0.000	0.010	0.000	0.000	0.005
Great Smoky Mountains NP, TN	Cold	0.006	0.042	0.047	0.021	0.005	0.016	0.043	0.056	0.069	0.005	0.058	0.026	0.005	0.048
Great Smoky Mountains NP, TN	Warm	0.000	0.013	0.010	0.006	0.000	0.003	0.010	0.012	0.017	0.000	0.019	0.005	0.000	0.013
Guadalupe Mountains NP, TX	Cold	0.000	0.014	0.019	0.006	0.001	0.004	0.011	0.011	0.016	0.000	0.016	0.006	0.000	0.008
Guadalupe Mountains NP, TX	Warm	0.000	0.005	0.009	0.003	0.000	0.001	0.004	0.003	0.005	0.000	0.008	0.002	0.000	0.003
Indian Gardens, AZ	Cold	0.002	0.013	0.031	0.009	0.001	0.003	0.011	0.023	0.023	0.003	0.021	0.010	0.000	0.019
Indian Gardens, AZ	Warm	0.000	0.008	0.023	0.007	0.000	0.002	0.004	0.006	0.006	0.000	0.019	0.002	0.000	0.005
Jarbridge Wilderness, NV	Cold	0.000	0.007	0.018	0.005	0.001	0.003	0.007	0.009	0.012	0.000	0.010	0.004	0.000	0.006
Jarbridge Wilderness, NV	Warm	0.000	0.006	0.011	0.005	0.001	0.005	0.010	0.010	0.016	0.001	0.017	0.004	0.002	0.011
Jefferson/James River Face, VA	Cold	0.022	0.122	0.088	0.125	0.056	0.179	0.371	0.486	0.644	0.083	0.446	0.448	0.061	0.458
Jefferson/James River Face, VA	Warm	0.003	0.028	0.020	0.013	0.004	0.011	0.032	0.056	0.086	0.009	0.072	0.041	0.008	0.099

Table A.2. Ambient Concentrations of Selected Fine Particle Chemical Species - Chiricahua to Jefferson/James (all values in ng/m³)

Site	Composite Sample	Benzo(ghi)perylene	Indeno(1,2,3-cd)fluoranthene	Dibenz[a,h]anthracene	Coronene	22,29,30-Trisnorhopane	22,29,30-Trisnorhopane	17a(H)-21b(H)-29-Norhopane	18a(H)-29-Norhopane	17b(H)-21a(H)-Normoreane	17a(H)-21b(H)-Hopane	17b(H),21a(H)-Moretane	22S, 17a(H),21b(H)-Homohopane	22R, 17a(H),21b(H)-Homohopane	22S, 17a(H),21b(H)-Bishomohopane
Chiricahua NM, AZ	Cold	0.007	0.002	0.000	0.030	0.006	0.006	0.023	0.008	0.000	0.034	0.000	0.012	0.009	0.007
Chiricahua NM, AZ	Warm	0.007	0.001	0.000	0.020	0.006	0.010	0.040	0.014	0.000	0.057	0.007	0.022	0.015	0.013
Columbia River Gorge, WA	Cold	0.954	0.162	0.148	0.896	0.049	0.057	0.215	0.066	0.000	0.325	0.040	0.140	0.118	0.087
Columbia River Gorge, WA	Warm	0.159	0.026	0.023	0.147	0.022	0.030	0.172	0.037	0.000	0.195	0.023	0.104	0.093	0.059
Crater Lake NP, OR	Cold	0.057	0.010	0.002	0.193	0.010	0.009	0.037	0.016	0.000	0.050	0.010	0.016	0.011	0.006
Crater Lake NP, OR	Warm	0.029	0.004	0.000	0.109	0.013	0.016	0.046	0.014	0.000	0.063	0.008	0.022	0.018	0.010
Denali NP, AK	Cold	0.015	0.004	0.000	0.037	0.009	0.013	0.040	0.010	0.000	0.049	0.000	0.017	0.014	0.009
Denali NP, AK	Warm	0.013	0.002	0.000	0.049	0.009	0.009	0.039	0.011	0.000	0.044	0.000	0.017	0.009	0.009
Dolly Sods Wilderness, WV	Cold	0.164	0.048	0.027	0.291	0.019	0.017	0.109	0.018	0.000	0.116	0.000	0.060	0.047	0.035
Dolly Sods Wilderness, WV	Warm	0.039	0.014	0.006	0.080	0.023	0.017	0.067	0.018	0.000	0.084	0.000	0.033	0.023	0.019
Gila Wilderness, NM	Cold	0.020	0.008	0.004	0.045	0.008	0.013	0.044	0.014	0.000	0.054	0.000	0.024	0.018	0.017
Gila Wilderness, NM	Warm	0.028	0.011	0.005	0.058	0.007	0.012	0.036	0.011	0.000	0.055	0.020	0.026	0.022	0.013
Glacier NP, MT	Cold	0.414	0.090	0.080	0.431	0.029	0.040	0.124	0.031	0.000	0.184	0.025	0.089	0.069	0.048
Glacier NP, MT	Warm	0.205	0.041	0.034	0.232	0.013	0.017	0.062	0.018	0.000	0.109	0.013	0.055	0.046	0.033
Grand Canyon NP, AZ	Cold	0.008	0.000	0.000	0.041	0.006	0.009	0.024	0.007	0.000	0.036	0.000	0.013	0.010	0.000
Grand Canyon NP, AZ	Warm	0.009	0.000	0.000	0.044	0.006	0.005	0.028	0.011	0.000	0.032	0.000	0.012	0.008	0.000
Great Basin NP, NV	Cold	0.024	0.009	0.003	0.051	0.007	0.007	0.027	0.008	0.000	0.032	0.000	0.011	0.008	0.000
Great Basin NP, NV	Warm	0.010	0.002	0.000	0.038	0.011	0.011	0.047	0.014	0.000	0.047	0.000	0.020	0.014	0.010
Great Gulf Wilderness, NH	Warm	0.039	0.010	0.004	0.094	0.014	0.015	0.067	0.026	0.000	0.072	0.000	0.024	0.018	0.000
Great Sand Dunes NM, CO	Cold	0.020	0.007	0.002	0.063	0.008	0.007	0.024	0.000	0.000	0.028	0.000	0.010	0.006	0.000
Great Sand Dunes NM, CO	Warm	0.013	0.003	0.000	0.047	0.012	0.011	0.039	0.011	0.000	0.050	0.000	0.017	0.012	0.009
Great Smoky Mountains NP, TN	Cold	0.000	0.021	0.009	0.196	0.018	0.020	0.080	0.013	0.000	0.083	0.000	0.047	0.039	0.026
Great Smoky Mountains NP, TN	Warm	0.017	0.006	0.002	0.039	0.009	0.013	0.037	0.014	0.000	0.046	0.000	0.021	0.019	0.015
Guadalupe Mountains NP, TX	Cold	0.018	0.004	0.000	0.049	0.018	0.014	0.079	0.023	0.000	0.093	0.000	0.043	0.042	0.025
Guadalupe Mountains NP, TX	Warm	0.007	0.001	0.000	0.018	0.010	0.009	0.034	0.012	0.000	0.046	0.008	0.020	0.016	0.016
Indian Gardens, AZ	Cold	0.026	0.008	0.003	0.060	0.011	0.012	0.054	0.015	0.000	0.061	0.009	0.022	0.020	0.012
Indian Gardens, AZ	Warm	0.018	0.002	0.000	0.032	0.011	0.012	0.051	0.019	0.000	0.062	0.000	0.025	0.021	0.014
Jarbridge Wilderness, NV	Cold	0.009	0.003	0.000	0.028	0.010	0.015	0.070	0.021	0.000	0.084	0.000	0.041	0.030	0.029
Jarbridge Wilderness, NV	Warm	0.017	0.005	0.002	0.063	0.008	0.011	0.046	0.013	0.000	0.073	0.010	0.029	0.025	0.017
Jefferson/James River Face, VA	Cold	0.513	0.172	0.074	0.924	0.024	0.040	0.148	0.025	0.000	0.164	0.016	0.079	0.067	0.043
Jefferson/James River Face, VA	Warm	0.110	0.041	0.018	0.266	0.016	0.012	0.058	0.017	0.002	0.088	0.000	0.055	0.053	0.037

Table A.2. Ambient Concentrations of Selected Fine Particle Chemical Species - Chiricahua to Jefferson/James (all values in ng/m³)

Site	Composite Sample	22R, 17a(H),21b(H)- Bishomohopane	22S, 17a(H),21b(H)- Trishomohopane	22R, 17a(H),21b(H)- Trishomohopane	20R+S, abb-Cholestane	20R, aaa-Cholestane	20R+S, abb-Ergostane	20R+S, abb-Sitostane	1H-Phenalen-1-one	Anthracen-9,10-dione	Benz(de)anthracen-7-one	Benz(a)anthracen-7,12- dione	Dibenzofuran	Squalene	Nonanal
Chiricahua NM, AZ	Cold	0.007	0.000	0.000	0.012	0.010	0.000	0.015	0.000	0.000	0.005	0.000	0.00	0.40	0.09
Chiricahua NM, AZ	Warm	0.010	0.008	0.003	0.029	0.015	0.000	0.019	0.000	0.000	0.000	0.000	0.00	1.03	0.00
Columbia River Gorge, WA	Cold	0.071	0.066	0.041	0.132	0.125	0.127	0.228	0.022	0.187	0.155	0.475	0.00	1.03	0.00
Columbia River Gorge, WA	Warm	0.050	0.046	0.028	0.060	0.050	0.043	0.099	0.000	0.019	0.008	0.000	0.00	0.60	0.28
Crater Lake NP, OR	Cold	0.006	0.000	0.000	0.018	0.021	0.000	0.023	0.009	0.007	0.016	0.000	0.00	0.79	0.00
Crater Lake NP, OR	Warm	0.011	0.006	0.000	0.035	0.025	0.000	0.027	0.000	0.000	0.000	0.000	0.00	0.60	0.12
Denali NP, AK	Cold	0.008	0.000	0.000	0.020	0.014	0.000	0.019	0.000	0.000	0.000	0.000	0.00	0.68	0.32
Denali NP, AK	Warm	0.006	0.000	0.000	0.018	0.016	0.000	0.017	0.000	0.000	0.000	0.000	0.00	0.69	0.00
Dolly Sods Wilderness, WV	Cold	0.020	0.019	0.012	0.034	0.021	0.000	0.045	0.068	0.034	0.234	0.079	0.00	1.45	0.00
Dolly Sods Wilderness, WV	Warm	0.014	0.014	0.014	0.029	0.026	0.000	0.040	0.000	0.000	0.050	0.025	0.00	0.07	0.00
Gila Wilderness, NM	Cold	0.016	0.014	0.009	0.021	0.013	0.000	0.017	0.000	0.000	0.015	0.000	0.00	0.67	0.38
Gila Wilderness, NM	Warm	0.012	0.014	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00	0.71	0.31
Glacier NP, MT	Cold	0.037	0.040	0.025	0.094	0.074	0.075	0.133	0.020	0.112	0.185	0.298	0.00	1.00	0.00
Glacier NP, MT	Warm	0.029	0.024	0.014	0.031	0.029	0.035	0.068	0.000	0.015	0.032	0.077	0.00	0.53	0.27
Grand Canyon NP, AZ	Cold	0.000	0.000	0.000	0.011	0.013	0.000	0.012	0.000	0.005	0.000	0.000	0.00	0.75	0.00
Grand Canyon NP, AZ	Warm	0.000	0.000	0.000	0.000	0.013	0.000	0.013	0.000	0.000	0.000	0.000	0.00	0.51	0.20
Great Basin NP, NV	Cold	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.012	0.006	0.038	0.008	0.00	0.73	0.00
Great Basin NP, NV	Warm	0.013	0.000	0.000	0.028	0.020	0.000	0.022	0.000	0.000	0.005	0.000	0.00	0.54	0.00
Great Gulf Wilderness, NH	Warm	0.000	0.000	0.000	0.032	0.032	0.000	0.031	0.000	0.000	0.012	0.000	0.00	0.49	0.44
Great Sand Dunes NM, CO	Cold	0.000	0.000	0.000	0.000	0.009	0.000	0.000	0.000	0.008	0.017	0.006	0.00	0.79	0.17
Great Sand Dunes NM, CO	Warm	0.011	0.000	0.000	0.022	0.013	0.000	0.019	0.000	0.000	0.000	0.000	0.00	0.55	0.16
Great Smoky Mountains NP, TN	Cold	0.022	0.026	0.000	0.027	0.019	0.000	0.038	0.000	0.021	0.045	0.000	0.00	1.17	0.31
Great Smoky Mountains NP, TN	Warm	0.016	0.013	0.000	0.000	0.000	0.000	0.018	0.000	0.000	0.000	0.000	0.00	0.31	0.00
Guadalupe Mountains NP, TX	Cold	0.018	0.000	0.000	0.028	0.031	0.000	0.041	0.000	0.006	0.000	0.000	0.00	1.07	0.19
Guadalupe Mountains NP, TX	Warm	0.010	0.007	0.006	0.022	0.018	0.000	0.013	0.000	0.000	0.000	0.000	0.00	0.70	0.00
Indian Gardens, AZ	Cold	0.011	0.000	0.000	0.033	0.026	0.000	0.032	0.000	0.000	0.025	0.000	0.00	1.23	0.17
Indian Gardens, AZ	Warm	0.014	0.012	0.000	0.027	0.016	0.000	0.019	0.000	0.000	0.000	0.000	0.00	0.75	0.26
Jarbridge Wilderness, NV	Cold	0.023	0.021	0.013	0.019	0.027	0.006	0.022	0.000	0.010	0.008	0.000	0.00	0.71	0.27
Jarbridge Wilderness, NV	Warm	0.017	0.012	0.008	0.019	0.024	0.023	0.046	0.000	0.000	0.011	0.000	0.00	0.77	0.21
Jefferson/James River Face, VA	Cold	0.048	0.043	0.022	0.071	0.049	0.000	0.090	0.159	0.104	0.947	0.173	0.00	1.00	0.24
Jefferson/James River Face, VA	Warm	0.029	0.026	0.018	0.000	0.000	0.000	0.040	0.000	0.014	0.083	0.037	0.00	0.78	0.00

Table A.2. Ambient Concentrations of Selected Fine Particle Chemical Species - Chiricahua to Jefferson/James (all values in ng/m³)

Site	Composite Sample	Levoglucosan	8,15-Pimaradienoic Acid	Pimaric Acid	Sandaracopimaric Acid	Isopimaric Acid	Dehydroabietic Acid	Abietic Acid	Abieta-6,8,11,13,15-pentatrien-18-oic Acid	Abieta-6,8,11,13-tetraen-18-oic Acid	Abieta-8,11,13,15-tetraen-18-oic Acid	7-Oxodehydroabietic Acid	Octanoic Acid	Nonanoic Acid	Decanoic Acid
Chiricahua NM, AZ	Cold	2.3	0.12	0.01	0.01	0.05	0.47	0.00	0.01	0.04	0.04	0.06	0.29	0.74	1.06
Chiricahua NM, AZ	Warm	1.8	0.01	0.02	0.01	0.06	0.29	0.00	0.01	0.05	0.03	0.08	0.24	0.59	0.84
Columbia River Gorge, WA	Cold	112.7	0.10	0.18	0.07	0.53	5.73	0.00	0.25	0.80	0.38	1.31	0.46	0.87	0.69
Columbia River Gorge, WA	Warm	29.5	0.10	0.04	0.03	0.36	1.85	0.00	0.13	0.28	0.12	0.49	0.73	1.10	1.02
Crater Lake NP, OR	Cold	7.1	0.05	0.10	0.02	0.03	1.36	0.00	0.00	0.36	0.10	0.19	0.32	1.27	1.06
Crater Lake NP, OR	Warm	10.8	0.05	0.09	0.03	0.23	1.56	0.00	0.00	0.27	0.08	0.20	0.41	0.73	0.91
Denali NP, AK	Cold	0.1	0.12	0.00	0.01	0.00	0.23	0.00	0.00	0.05	0.00	0.02	0.27	0.97	1.09
Denali NP, AK	Warm	1.5	0.01	0.01	0.00	0.05	0.22	0.00	0.00	0.03	0.01	0.03	0.73	0.97	1.24
Dolly Sods Wilderness, WV	Cold	194.5	0.06	0.04	0.00	0.00	0.64	0.00	0.00	0.00	0.00	0.12	0.15	0.27	0.47
Dolly Sods Wilderness, WV	Warm	0.0	0.00	0.00	0.00	0.00	0.55	0.00	0.00	0.00	0.00	0.13	0.00	0.00	0.00
Gila Wilderness, NM	Cold	37.8	1.13	1.20	0.31	1.83	18.82	0.48	0.18	5.04	1.54	1.80	0.24	0.73	0.87
Gila Wilderness, NM	Warm	55.2	0.75	0.95	0.32	1.41	27.64	0.19	0.21	6.15	2.29	4.51	0.23	0.48	0.61
Glacier NP, MT	Cold	146.6	0.34	0.88	0.23	1.79	16.65	0.19	0.37	3.49	1.98	1.90	0.11	0.39	0.55
Glacier NP, MT	Warm	62.4	0.14	0.31	0.09	0.89	8.18	0.06	0.18	1.04	0.45	1.33	0.22	0.36	0.58
Grand Canyon NP, AZ	Cold	2.2	0.18	0.04	0.02	0.06	2.47	0.00	0.00	0.22	0.07	0.14	0.34	0.75	1.12
Grand Canyon NP, AZ	Warm	2.1	0.21	0.07	0.02	0.14	2.25	0.00	0.01	0.34	0.11	0.28	0.24	0.67	0.80
Great Basin NP, NV	Cold	5.2	10.18	0.03	0.30	0.74	4.59	0.04	0.05	0.97	0.35	0.45	0.33	0.90	1.18
Great Basin NP, NV	Warm	3.3	0.83	0.01	0.03	0.11	0.63	0.00	0.00	0.11	0.04	0.07	0.30	0.77	1.03
Great Gulf Wilderness, NH	Warm	83.4	0.04	0.02	0.02	0.60	0.92	0.00	0.03	0.21	0.17	0.26	0.36	0.58	0.62
Great Sand Dunes NM, CO	Cold	7.2	0.50	0.03	0.04	0.16	0.76	0.00	0.01	0.17	0.07	0.11	0.31	0.96	1.39
Great Sand Dunes NM, CO	Warm	4.2	0.05	0.03	0.01	0.08	0.49	0.00	0.00	0.09	0.04	0.12	0.32	0.78	1.11
Great Smoky Mountains NP, TN	Cold	74.6	0.04	0.07	0.03	0.17	1.93	0.00	0.07	0.33	0.16	0.45	0.28	0.49	0.75
Great Smoky Mountains NP, TN	Warm	0.0	0.00	0.02	0.00	0.15	0.66	0.00	0.09	0.52	0.12	0.51	0.10	0.63	0.53
Guadalupe Mountains NP, TX	Cold	9.3	0.04	0.01	0.01	0.07	1.04	0.00	0.03	0.08	0.08	0.08	0.53	1.51	2.24
Guadalupe Mountains NP, TX	Warm	1.7	0.00	0.00	0.00	0.05	0.18	0.00	0.00	0.02	0.01	0.03	0.24	0.70	0.97
Indian Gardens, AZ	Cold	7.1	0.70	0.03	0.04	0.13	0.98	0.00	0.02	0.17	0.12	0.14	0.27	0.54	0.82
Indian Gardens, AZ	Warm	5.0	0.36	0.06	0.04	0.15	1.88	0.00	0.01	0.32	0.19	0.35	2.59	1.88	1.89
Jarbridge Wilderness, NV	Cold	5.7	0.04	0.02	0.01	0.00	0.29	0.00	0.00	0.08	0.04	0.06	0.27	0.91	1.37
Jarbridge Wilderness, NV	Warm	32.4	0.00	0.03	0.01	0.15	0.63	0.00	0.01	0.11	0.04	0.12	0.37	0.81	0.92
Jefferson/James River Face, VA	Cold	329.0	0.17	0.38	0.16	0.78	8.16	0.19	0.17	1.58	0.64	0.89	0.15	0.37	0.42
Jefferson/James River Face, VA	Warm	122.1	0.04	0.10	0.04	0.30	2.88	0.00	0.17	1.06	0.28	0.64	0.09	0.23	0.45

Table A.2. Ambient Concentrations of Selected Fine Particle Chemical Species - Chiricahua to Jefferson/James - Chiricahua to Jefferson/James (all values in ng/m³)

Site	Composite Sample	Undecanoic Acid	Dodecanoic Acid	Tridecanoic Acid	Tetradecanoic Acid	Pentadecanoic Acid	Hexadecanoic Acid	Heptadecanoic Acid	Octadecanoic Acid	Nonadecanoic Acid	Eicosanoic Acid	Henicosanoic Acid	Docosanoic Acid	Tricosanoic Acid	Tetracosanoic Acid
Chiricahua NM, AZ	Cold	0.19	1.51	0.26	1.75	0.70	4.29	0.25	3.08	0.05	0.25	0.07	0.47	0.15	0.63
Chiricahua NM, AZ	Warm	0.18	1.46	0.29	1.80	0.85	6.13	0.36	3.29	0.11	0.42	0.14	0.87	0.28	1.13
Columbia River Gorge, WA	Cold	0.13	1.65	0.28	2.41	1.52	13.09	0.72	6.08	0.33	2.25	0.56	6.66	0.91	7.03
Columbia River Gorge, WA	Warm	0.19	1.80	0.34	2.84	1.74	13.44	0.85	6.60	0.41	2.38	0.58	5.79	0.91	6.97
Crater Lake NP, OR	Cold	0.18	2.05	0.31	4.14	0.99	7.86	0.27	4.87	0.09	0.32	0.00	0.75	0.07	0.79
Crater Lake NP, OR	Warm	0.16	1.40	0.29	2.55	1.11	8.37	0.50	4.07	0.19	1.06	0.28	1.96	0.44	1.93
Denali NP, AK	Cold	0.13	1.74	0.21	2.16	0.69	5.95	0.24	3.33	0.03	0.12	0.00	0.20	0.00	0.17
Denali NP, AK	Warm	0.17	1.79	0.29	2.92	1.45	9.24	0.48	3.40	0.08	0.36	0.09	0.47	0.14	0.52
Dolly Sods Wilderness, WV	Cold	0.10	1.45	0.31	2.59	1.62	9.77	0.74	5.16	0.37	1.14	0.00	3.56	0.99	3.02
Dolly Sods Wilderness, WV	Warm	0.00	0.00	0.00	2.28	2.44	10.99	0.00	6.09	0.00	1.94	0.00	3.70	0.59	2.66
Gila Wilderness, NM	Cold	0.14	1.66	0.25	1.89	0.85	5.52	0.39	3.97	0.19	1.90	0.34	3.93	0.77	3.75
Gila Wilderness, NM	Warm	0.14	1.42	0.26	1.78	0.87	6.69	0.53	4.83	0.48	4.10	0.91	11.48	2.09	11.76
Glacier NP, MT	Cold	0.11	1.62	0.33	2.37	1.14	8.30	0.49	5.40	0.22	2.19	0.00	5.80	0.45	4.73
Glacier NP, MT	Warm	0.10	1.08	0.24	2.09	1.06	8.18	0.57	4.55	0.42	3.34	0.69	6.71	1.25	5.85
Grand Canyon NP, AZ	Cold	0.17	2.05	0.30	1.99	0.87	4.49	0.26	3.18	0.05	0.28	0.06	0.52	0.14	0.55
Grand Canyon NP, AZ	Warm	0.14	1.66	0.27	2.17	1.07	6.53	0.38	3.32	0.11	0.66	0.17	1.42	0.36	1.45
Great Basin NP, NV	Cold	0.19	2.38	0.32	1.95	0.84	5.16	0.30	3.54	0.08	0.56	0.13	1.27	0.20	1.54
Great Basin NP, NV	Warm	0.18	1.92	0.32	2.32	1.09	6.54	0.34	3.26	0.10	0.42	0.13	0.98	0.23	0.95
Great Gulf Wilderness, NH	Warm	0.15	1.34	0.28	2.09	1.18	12.17	0.73	6.85	0.71	5.76	1.22	7.61	1.82	6.02
Great Sand Dunes NM, CO	Cold	0.22	2.33	0.34	2.10	0.90	6.20	0.35	3.87	0.09	0.74	0.21	1.70	0.42	2.21
Great Sand Dunes NM, CO	Warm	0.18	1.94	0.33	2.31	0.91	6.02	0.35	3.68	0.10	0.56	0.14	1.06	0.27	1.26
Great Smoky Mountains NP, TN	Cold	0.14	1.54	0.24	1.88	0.90	7.62	0.43	4.74	0.20	0.92	0.50	2.49	1.06	4.13
Great Smoky Mountains NP, TN	Warm	0.00	1.05	0.22	1.43	0.84	8.85	0.44	4.67	0.20	1.78	0.39	2.59	0.80	2.99
Guadalupe Mountains NP, TX	Cold	0.32	2.89	0.45	3.13	1.33	8.98	0.55	5.80	0.12	0.72	0.21	1.19	0.50	1.57
Guadalupe Mountains NP, TX	Warm	0.17	1.83	0.29	2.15	1.03	8.25	0.50	4.90	0.10	0.53	0.14	0.63	0.29	1.06
Indian Gardens, AZ	Cold	0.13	1.74	0.28	2.29	1.08	7.57	0.42	4.08	0.09	0.46	0.14	1.07	0.37	1.33
Indian Gardens, AZ	Warm	0.22	2.52	0.32	2.38	1.17	9.97	0.52	5.27	0.16	0.84	0.24	1.15	0.48	2.08
Jarbridge Wilderness, NV	Cold	0.19	1.91	0.25	2.85	1.07	6.13	0.31	4.00	0.04	0.32	0.00	0.64	0.14	0.63
Jarbridge Wilderness, NV	Warm	0.16	1.62	0.30	2.75	1.15	8.78	0.49	4.63	0.16	1.09	0.30	2.00	0.63	2.18
Jefferson/James River Face, VA	Cold	0.09	1.16	0.33	1.93	1.20	10.49	0.90	6.24	0.65	3.02	1.88	10.88	3.06	14.88
Jefferson/James River Face, VA	Warm	0.07	1.22	0.25	1.55	0.89	9.36	0.59	5.56	0.23	1.71	0.54	3.66	1.06	4.80

Table A.2. Ambient Concentrations of Selected Fine Particle Chemical Species - Chiricahua to Jefferson/James (all values in ng/m³)

Site	Composite Sample	Pentacosanoic Acid	Hexacosanoic Acid	Heptacosanoic Acid	Octacosanoic Acid	Nonacosanoic Acid	Triacontanoic Acid	Hentriacontanoic Acid	Dotriacontanoic Acid	9-Hexadecenoic Acid	9,12-Octadecanedienoic Acid	9-Octadecenoic Acid	Propanedioic Acid	Methylpropanedioic Acid	Butanedioic Acid
Chiricahua NM, AZ	Cold	0.10	0.35	0.06	0.30	0.03	0.21	0.01	0.07	1.83	0.26	1.26	0.34	0.00	2.46
Chiricahua NM, AZ	Warm	0.19	0.59	0.12	0.71	0.10	0.69	0.04	0.21	1.58	0.36	1.47	0.76	0.18	5.57
Columbia River Gorge, WA	Cold	0.39	2.12	0.10	0.47	0.05	0.30	0.00	0.07	1.69	0.38	1.83	0.42	0.00	8.33
Columbia River Gorge, WA	Warm	0.48	2.44	0.20	1.08	0.13	0.75	0.05	0.22	1.87	0.55	1.43	0.00	0.00	4.97
Crater Lake NP, OR	Cold	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.00	1.64	0.29	0.92	0.00	0.00	0.00
Crater Lake NP, OR	Warm	0.24	0.71	0.10	0.40	0.07	0.28	0.02	0.09	1.88	0.67	1.59	0.82	0.00	6.67
Denali NP, AK	Cold	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.20	0.07	0.75	0.00	0.00	0.62
Denali NP, AK	Warm	0.10	0.28	0.03	0.15	0.01	0.06	0.00	0.01	2.52	1.76	2.02	0.00	0.00	1.56
Dolly Sods Wilderness, WV	Cold	0.47	1.03	0.09	0.35	0.00	0.19	0.00	0.00	3.67	0.39	2.39	3.21	0.00	11.68
Dolly Sods Wilderness, WV	Warm	0.00	1.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.18	6.57	0.00	2.42
Gila Wilderness, NM	Cold	0.29	0.93	0.08	0.42	0.06	0.29	0.02	0.10	1.72	0.39	1.51	0.30	0.00	3.64
Gila Wilderness, NM	Warm	0.80	2.80	0.27	1.38	0.20	1.28	0.07	0.39	1.67	0.65	1.39	1.55	0.00	9.17
Glacier NP, MT	Cold	0.16	0.72	0.00	0.00	0.00	0.00	0.00	0.00	1.78	0.34	1.61	0.77	0.00	6.92
Glacier NP, MT	Warm	0.56	1.92	0.24	0.98	0.13	0.71	0.06	0.23	1.21	1.64	1.50	0.68	0.00	6.87
Grand Canyon NP, AZ	Cold	0.08	0.22	0.04	0.16	0.02	0.12	0.00	0.03	1.59	0.25	1.09	0.18	0.00	1.98
Grand Canyon NP, AZ	Warm	0.18	0.55	0.11	0.55	0.07	0.45	0.02	0.09	1.71	0.24	1.56	0.82	0.00	4.39
Great Basin NP, NV	Cold	0.11	0.52	0.03	0.15	0.02	0.07	0.00	0.03	1.63	0.22	1.32	0.00	0.00	1.78
Great Basin NP, NV	Warm	0.14	0.42	0.08	0.39	0.05	0.30	0.01	0.06	1.42	0.27	1.30	0.49	0.00	2.88
Great Gulf Wilderness, NH	Warm	0.82	2.41	0.42	1.96	0.24	0.99	0.08	0.34	1.55	2.30	2.31	8.96	0.64	18.77
Great Sand Dunes NM, CO	Cold	0.21	0.72	0.06	0.30	0.03	0.22	0.00	0.07	1.91	0.25	1.48	0.00	0.00	1.54
Great Sand Dunes NM, CO	Warm	0.17	0.58	0.09	0.59	0.07	0.47	0.02	0.14	1.67	0.41	1.40	0.00	0.00	5.96
Great Smoky Mountains NP, TN	Cold	0.53	2.21	0.22	1.25	0.20	1.09	0.09	0.43	1.97	0.43	1.61	1.09	0.00	8.96
Great Smoky Mountains NP, TN	Warm	0.48	1.73	0.29	1.55	0.22	1.23	0.09	0.42	0.34	0.41	0.64	16.61	0.00	11.90
Guadalupe Mountains NP, TX	Cold	0.33	1.06	0.24	1.53	0.23	1.63	0.12	0.71	2.33	0.33	2.13	0.75	0.00	4.66
Guadalupe Mountains NP, TX	Warm	0.22	0.72	0.18	1.29	0.16	1.38	0.07	0.47	1.80	0.20	1.45	0.92	0.00	3.45
Indian Gardens, AZ	Cold	0.20	0.71	0.07	0.43	0.04	0.19	0.01	0.04	2.47	0.36	2.33	0.19	0.00	1.98
Indian Gardens, AZ	Warm	0.29	0.83	0.18	0.96	0.13	0.86	0.04	0.19	1.87	0.49	1.73	0.00	0.00	1.61
Jarbridge Wilderness, NV	Cold	0.07	0.18	0.00	0.00	0.00	0.00	0.00	0.00	1.64	0.25	1.10	0.34	0.00	1.81
Jarbridge Wilderness, NV	Warm	0.32	1.05	0.14	0.72	0.10	0.46	0.03	0.10	2.20	0.30	1.40	0.63	0.00	5.80
Jefferson/James River Face, VA	Cold	1.24	7.38	0.35	1.68	0.19	1.10	0.09	0.45	1.44	0.69	1.36	1.91	0.16	13.17
Jefferson/James River Face, VA	Warm	0.51	2.35	0.23	1.22	0.15	0.83	0.07	0.29	2.56	6.21	2.99	15.76	0.00	24.37

Table A.2. Ambient Concentrations of Selected Fine Particle Chemical Species - Chiricahua to Jefferson/James (all values in ng/m³)

Site	Composite Sample	Methylbutanedioic Acid	Pentanedioic Acid	Hexanedioic Acid	Heptanedioic Acid	Octanedioic Acid	Nonanedioic Acid
Chiricahua NM, AZ	Cold	0.31	0.72	1.20	0.24	0.48	0.97
Chiricahua NM, AZ	Warm	0.52	1.42	1.66	0.53	0.71	1.30
Columbia River Gorge, WA	Cold	1.61	2.40	1.78	2.60	1.56	4.19
Columbia River Gorge, WA	Warm	0.75	1.65	2.16	0.64	1.75	3.42
Crater Lake NP, OR	Cold	0.00	0.00	0.00	0.00	0.00	0.00
Crater Lake NP, OR	Warm	0.67	1.92	1.61	0.66	1.65	2.84
Denali NP, AK	Cold	0.00	0.00	2.31	0.00	0.00	0.00
Denali NP, AK	Warm	0.17	0.48	1.23	0.28	0.73	1.34
Dolly Sods Wilderness, WV	Cold	3.23	3.58	4.45	0.86	1.56	3.14
Dolly Sods Wilderness, WV	Warm	0.18	0.43	1.82	0.00	0.00	0.23
Gila Wilderness, NM	Cold	0.63	1.03	0.97	0.32	1.01	2.38
Gila Wilderness, NM	Warm	1.45	2.59	1.80	0.94	1.82	5.03
Glacier NP, MT	Cold	2.20	1.58	1.24	0.00	0.86	3.85
Glacier NP, MT	Warm	1.00	2.36	1.89	0.78	2.05	4.12
Grand Canyon NP, AZ	Cold	0.28	0.69	1.09	0.22	0.60	0.99
Grand Canyon NP, AZ	Warm	0.43	1.28	1.03	0.41	0.74	1.47
Great Basin NP, NV	Cold	0.32	0.52	1.22	0.20	0.39	1.41
Great Basin NP, NV	Warm	0.30	0.77	1.02	0.32	0.60	1.21
Great Gulf Wilderness, NH	Warm	1.52	4.70	4.48	1.56	3.16	6.25
Great Sand Dunes NM, CO	Cold	0.32	0.56	0.98	0.25	0.53	2.42
Great Sand Dunes NM, CO	Warm	0.55	1.62	1.58	0.63	1.06	2.01
Great Smoky Mountains NP, TN	Cold	1.47	2.81	2.60	0.86	1.81	3.76
Great Smoky Mountains NP, TN	Warm	0.63	2.17	4.98	0.67	0.76	1.70
Guadalupe Mountains NP, TX	Cold	0.65	1.45	2.61	0.28	0.85	1.82
Guadalupe Mountains NP, TX	Warm	0.34	0.88	1.59	0.17	0.74	1.38
Indian Gardens, AZ	Cold	0.30	0.56	0.90	0.13	0.47	1.31
Indian Gardens, AZ	Warm	0.24	0.77	2.55	0.32	0.80	2.44
Jarbridge Wilderness, NV	Cold	0.10	0.36	0.70	0.00	0.34	1.00
Jarbridge Wilderness, NV	Warm	0.77	1.67	1.41	0.61	1.15	2.58
Jefferson/James River Face, VA	Cold	2.98	4.92	3.79	1.09	2.06	7.51
Jefferson/James River Face, VA	Warm	1.70	6.81	11.77	1.52	2.77	7.03

Table A.3. Ambient Concentrations of Selected Fine Particle Chemical Species - Kenmore to Redwood (all values in ng/m³)

Site	Composite Sample	Total Carbon	Silicon	Aluminum	Potassium	Guaiacyl Acetone	Acetovanillone	Vanillin	Syringaldehyde	Homovanillic Acid	Vanillic Acid	Sinapyl Aldehyde	Syringic Acid	Syringyl Acetone	Propionyl Syringol
Kenmore Square, Boston, MA	Cold	6655	161	55	0	0.00	0.60	4.89	0.00	0.00	0.00	0.00	5.58	0.00	0.00
Kenmore Square, Boston, MA	Warm	6935	144	48	0	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lassen Volcanic NP, CA	Cold	709	66	28	11	0.00	0.00	0.04	0.06	0.00	0.00	0.00	0.00	0.00	0.01
Lassen Volcanic NP, CA	Warm	1151	131	71	12	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lone Peak Wilderness, UT	Cold	913	86	41	1	0.00	0.00	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lone Peak Wilderness, UT	Warm	1346	193	74	17	0.11	0.04	0.28	0.47	0.00	0.00	0.00	0.00	0.17	0.10
Lye Brook Wilderness, VT	Cold	770	36	16	14	0.00	0.00	0.04	0.12	0.00	0.00	0.00	0.00	0.00	0.07
Lye Brook Wilderness, VT	Warm	1602	59	23	15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mammoth Cave NP, KY	Cold	1973	82	38	32	0.09	0.03	0.24	0.36	0.00	0.00	0.00	2.23	0.22	0.23
Mammoth Cave NP, KY	Warm	2748	144	51	32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mesa Verde NP, CO	Cold	481	97	40	7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mesa Verde NP, CO	Warm	769	165	65	14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Moosehorn NWR, ME	Cold	1269	35	20	52	0.06	0.02	0.18	0.63	0.00	0.00	0.00	0.00	0.00	0.36
Moosehorn NWR, ME	Warm	1765	47	17	54	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mount Ranier NP, WA	Cold	1271	32	13	19	0.23	0.10	0.54	1.00	1.06	1.47	0.00	2.15	0.32	0.35
Mount Ranier NP, WA	Warm	1941	56	22	26	0.14	0.05	0.18	0.06	0.00	0.00	0.00	0.78	0.05	0.05
Mount Zirkel Wilderness, CO	Cold	408	64	29	4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mount Zirkel Wilderness, CO	Warm	652	172	70	10	0.00	0.00	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00
Okefenokee NWR, GA	Cold	2187	58	27	37	0.00	0.04	0.16	0.04	0.00	0.52	0.00	1.21	0.06	0.04
Okefenokee NWR, GA	Warm	2164	203	99	28	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Petrified Forest NP, AZ	Cold	868	109	46	4	0.00	0.02	0.08	0.04	0.00	0.00	0.00	0.00	0.00	0.00
Petrified Forest NP, AZ	Warm	1066	219	84	18	0.00	0.00	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Pinnacles NM, CA	Cold	1590	53	17	28	0.13	0.03	0.28	0.55	0.00	0.41	0.00	2.20	0.29	0.43
Pinnacles NM, CA	Warm	1711	139	29	32	0.04	0.00	0.04	0.06	0.00	0.00	0.00	0.00	0.04	0.04
Point Reyes National Seashore, CA	Cold	1113	32	9	28	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Point Reyes National Seashore, CA	Warm	644	34	6	35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Quabbin Reservoir, MA	Cold	2545	101	43	0	0.19	0.26	3.73	2.22	0.00	0.00	0.00	0.00	0.26	0.50
Quabbin Reservoir, MA	Warm	3583	78	29	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Reading, MA	Cold	4722	139	50	0	0.49	0.84	9.85	2.49	0.00	0.00	0.00	2.24	0.48	0.91
Reading, MA	Warm	4475	119	57	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Redwood NP, CA	Cold	787	27	11	24	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.02
Redwood NP, CA	Warm	990	32	7	35	0.07	0.00	0.19	0.08	0.00	0.00	0.00	0.00	0.02	0.03

Table A.3. Ambient Concentrations of Selected Fine Particle Chemical Species - Kenmore to Redwood (all values in ng/m³)

Site	Composite Sample	Acetosyringone	Acetonylsyringol	Juvabione	Dehydrojuvabione	Beta-Sitosterol	Stigmast-4-en-3-one	Stigmasta-3,5-dien-7-one	Stigmasta-4,6-dien-3-one	Stigmastan-3-ol	Stigmastan-3-one	Friedelin	Beta-Amyrone	Beta-Amyrin	Alpha-Amyrone
Kenmore Square, Boston, MA	Cold	0.27	0.00	0.00	0.00	0.72	0.25	0.11	0.06	0.11	0.05	0.38	0.02	0.02	0.04
Kenmore Square, Boston, MA	Warm	0.00	0.00	0.00	0.00	0.24	0.06	0.06	0.00	0.00	0.00	0.16	0.00	0.01	0.01
Lassen Volcanic NP, CA	Cold	0.06	0.00	0.00	0.00	0.09	0.04	0.02	0.00	0.04	0.02	0.00	0.00	0.00	0.00
Lassen Volcanic NP, CA	Warm	0.04	0.03	0.00	0.00	0.13	0.07	0.04	0.02	0.05	0.02	0.04	0.00	0.00	0.00
Lone Peak Wilderness, UT	Cold	0.04	0.00	0.00	0.00	0.19	0.09	0.04	0.03	0.06	0.00	0.07	0.01	0.01	0.03
Lone Peak Wilderness, UT	Warm	0.19	0.20	0.06	0.00	0.57	0.31	0.09	0.04	0.14	0.09	0.12	0.03	0.03	0.09
Lye Brook Wilderness, VT	Cold	0.18	0.05	0.00	0.00	0.13	0.03	0.01	0.00	0.00	0.03	0.06	0.00	0.00	0.00
Lye Brook Wilderness, VT	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Mammoth Cave NP, KY	Cold	0.43	0.28	0.00	0.00	0.28	0.21	0.06	0.04	0.08	0.06	0.42	0.01	0.02	0.02
Mammoth Cave NP, KY	Warm	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mesa Verde NP, CO	Cold	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mesa Verde NP, CO	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Moosehorn NWR, ME	Cold	0.85	0.20	0.24	0.07	0.26	0.17	0.05	0.03	0.10	0.05	0.07	0.01	0.01	0.02
Moosehorn NWR, ME	Warm	0.00	0.00	0.19	0.00	0.00	0.17	0.14	0.03	0.00	0.04	0.11	0.01	0.01	0.03
Mount Ranier NP, WA	Cold	0.73	0.43	0.05	0.00	0.52	0.37	0.09	0.06	0.20	0.16	0.12	0.02	0.01	0.05
Mount Ranier NP, WA	Warm	0.10	0.11	0.00	0.00	0.20	0.22	0.06	0.00	0.07	0.09	0.00	0.02	0.01	0.03
Mount Zirkel Wilderness, CO	Cold	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mount Zirkel Wilderness, CO	Warm	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Okefenokee NWR, GA	Cold	0.09	0.10	0.00	0.00	0.19	0.41	0.10	0.05	0.11	0.03	0.31	0.02	0.02	0.06
Okefenokee NWR, GA	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Petrified Forest NP, AZ	Cold	0.00	0.00	0.00	0.00	0.08	0.05	0.02	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Petrified Forest NP, AZ	Warm	0.00	0.00	0.00	0.00	0.05	0.05	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pinnacles NM, CA	Cold	0.77	0.35	0.00	0.00	0.48	0.28	0.13	0.06	0.11	0.04	0.64	0.01	0.02	0.03
Pinnacles NM, CA	Warm	0.08	0.05	0.00	0.00	0.08	0.09	0.04	0.02	0.04	0.01	0.18	0.01	0.01	0.01
Point Reyes National Seashore, CA	Cold	0.04	0.00	0.00	0.00	0.16	0.09	0.04	0.01	0.00	0.00	0.44	0.00	0.01	0.01
Point Reyes National Seashore, CA	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Quabbin Reservoir, MA	Cold	0.94	0.33	0.00	0.00	0.41	0.25	0.08	0.04	0.15	0.08	0.32	0.01	0.01	0.03
Quabbin Reservoir, MA	Warm	0.00	0.00	0.00	0.00	0.00	0.05	0.06	0.00	0.00	0.00	0.19	0.00	0.01	0.02
Reading, MA	Cold	1.70	0.61	0.00	0.00	0.74	0.46	0.14	0.08	0.20	0.12	0.39	0.02	0.02	0.04
Reading, MA	Warm	0.00	0.00	0.00	0.00	0.20	0.12	0.10	0.00	0.00	0.04	0.25	0.01	0.01	0.02
Redwood NP, CA	Cold	0.07	0.05	0.00	0.00	0.12	0.10	0.03	0.00	0.00	0.04	1.07	0.02	0.01	0.02
Redwood NP, CA	Warm	0.08	0.05	0.00	0.00	0.20	0.15	0.06	0.03	0.05	0.04	0.69	0.02	0.01	0.03

Table A.3. Ambient Concentrations of Selected Fine Particle Chemical Species - Kenmore to Redwood (all values in ng/m³)

Site	Composite Sample	Alpha-Amyrin	Alpha-Tocopherol	Delta-Tocopherol	Beta-Tocopherol	Betulin	Cholesterol	Hexadecane	Heptadecane	Octadecane	Nonadecane	Eicosane	Henicosane	Docosane	Tricosane
Kenmore Square, Boston, MA	Cold	0.03	0.00	0.00	0.00	0.00	0.96	0.00	1.00	1.89	3.52	4.10	4.20	3.62	2.82
Kenmore Square, Boston, MA	Warm	0.02	0.00	0.00	0.00	0.00	0.41	0.00	0.34	0.00	0.59	0.75	1.39	1.64	2.75
Lassen Volcanic NP, CA	Cold	0.00	0.00	0.00	0.00	0.00	0.34	0.00	0.00	0.00	0.00	0.08	0.10	0.18	0.34
Lassen Volcanic NP, CA	Warm	0.00	0.00	0.00	0.00	0.00	0.31	0.00	0.00	0.00	0.00	0.09	0.14	0.18	0.50
Lone Peak Wilderness, UT	Cold	0.02	0.00	0.00	0.00	0.00	0.33	0.00	0.00	0.00	0.00	0.11	0.15	0.20	0.29
Lone Peak Wilderness, UT	Warm	0.09	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00	0.09	0.11	0.13	0.28
Lye Brook Wilderness, VT	Cold	0.00	0.00	0.00	0.00	0.00	0.26	0.05	0.00	0.00	0.00	0.08	0.14	0.19	0.29
Lye Brook Wilderness, VT	Warm	0.01	0.00	0.00	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.08	0.09	0.12	0.29
Mammoth Cave NP, KY	Cold	0.03	0.04	0.00	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.07	0.10	0.16	0.30
Mammoth Cave NP, KY	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.06	0.10	0.20
Mesa Verde NP, CO	Cold	0.00	0.00	0.00	0.00	0.00	0.20	0.00	0.00	0.00	0.00	0.11	0.18	0.25	0.32
Mesa Verde NP, CO	Warm	0.00	0.00	0.00	0.00	0.00	0.23	0.00	0.00	0.00	0.00	0.07	0.13	0.20	0.42
Moosehorn NWR, ME	Cold	0.03	0.00	0.00	0.00	0.00	0.19	0.00	0.00	0.00	0.00	0.09	0.21	0.46	0.76
Moosehorn NWR, ME	Warm	0.02	0.00	0.00	0.00	0.00	0.26	0.00	0.00	0.00	0.00	0.10	0.08	0.14	0.35
Mount Ranier NP, WA	Cold	0.04	0.03	0.00	0.00	0.00	0.26	0.00	0.11	0.12	0.00	0.00	0.15	0.23	0.41
Mount Ranier NP, WA	Warm	0.02	0.00	0.00	0.00	0.00	0.29	0.00	0.00	0.06	0.00	0.09	0.12	0.19	0.40
Mount Zirkel Wilderness, CO	Cold	0.00	0.00	0.00	0.00	0.00	0.23	0.00	0.00	0.06	0.00	0.09	0.14	0.19	0.40
Mount Zirkel Wilderness, CO	Warm	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.09	0.12	0.20	0.38
Okefenokee NWR, GA	Cold	0.05	0.03	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.05	0.08	0.12	0.21
Okefenokee NWR, GA	Warm	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.07	0.10	0.20
Petrified Forest NP, AZ	Cold	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.10	0.15	0.24	0.40
Petrified Forest NP, AZ	Warm	0.00	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.00	0.07	0.11	0.17	0.38
Pinnacles NM, CA	Cold	0.02	0.01	0.00	0.00	0.00	0.23	0.00	0.00	0.00	0.00	0.07	0.10	0.19	0.43
Pinnacles NM, CA	Warm	0.02	0.00	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.08	0.12	0.18	0.40
Point Reyes National Seashore, CA	Cold	0.01	0.00	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.05	0.07	0.10	0.20
Point Reyes National Seashore, CA	Warm	0.00	0.00	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.00	0.05	0.06	0.10	0.20
Quabbin Reservoir, MA	Cold	0.03	0.00	0.00	0.00	0.00	0.42	0.00	0.30	0.29	0.34	0.40	0.76	1.49	2.29
Quabbin Reservoir, MA	Warm	0.01	0.00	0.00	0.00	0.00	0.29	0.00	0.14	0.18	0.31	0.38	0.85	1.05	3.26
Reading, MA	Cold	0.04	0.00	0.00	0.00	0.00	0.57	0.00	0.46	0.83	1.21	1.40	1.65	1.65	1.70
Reading, MA	Warm	0.01	0.00	0.00	0.00	0.00	0.38	0.05	0.17	0.30	0.31	0.36	0.66	0.71	1.70
Redwood NP, CA	Cold	0.02	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.04	0.05	0.12
Redwood NP, CA	Warm	0.03	0.01	0.00	0.00	0.00	0.19	0.00	0.00	0.00	0.00	0.07	0.11	0.14	0.29

Table A.3. Ambient Concentrations of Selected Fine Particle Chemical Species - Kenmore to Redwood (all values in ng/m³)

Site	Composite Sample	Tetracosane	Pentacosane	Hexacosane	Heptacosane	Octacosane	Nonacosane	Triacosane	Hentriacontane	Dotriacontane	Tritriacontane	Tetratriacontane	Pentatriacontane	Hexatriacontane	Fluoranthene
Kenmore Square, Boston, MA	Cold	2.29	2.10	1.14	0.98	0.66	1.24	0.59	1.10	0.41	0.48	0.00	0.00	0.00	1.396
Kenmore Square, Boston, MA	Warm	1.73	2.15	0.98	1.31	0.54	1.40	0.53	1.36	0.35	0.48	0.00	0.00	0.00	0.197
Lassen Volcanic NP, CA	Cold	0.48	0.61	0.44	0.50	0.31	0.53	0.24	0.34	0.14	0.11	0.08	0.00	0.00	0.005
Lassen Volcanic NP, CA	Warm	0.51	0.78	0.47	0.72	0.31	0.93	0.20	0.49	0.11	0.13	0.06	0.06	0.00	0.003
Lone Peak Wilderness, UT	Cold	0.38	0.43	0.31	0.34	0.20	0.34	0.15	0.26	0.09	0.09	0.00	0.00	0.00	0.052
Lone Peak Wilderness, UT	Warm	0.38	0.75	0.49	1.09	0.45	1.53	0.41	0.94	0.30	0.32	0.22	0.15	0.00	0.027
Lye Brook Wilderness, VT	Cold	0.35	0.37	0.26	0.27	0.14	0.30	0.14	0.21	0.10	0.11	0.00	0.00	0.00	0.030
Lye Brook Wilderness, VT	Warm	0.29	0.65	0.38	0.69	0.28	0.67	0.26	0.59	0.17	0.18	0.00	0.00	0.00	0.010
Mammoth Cave NP, KY	Cold	0.36	0.65	0.42	0.56	0.28	0.82	0.23	0.70	0.15	0.15	0.00	0.00	0.00	0.047
Mammoth Cave NP, KY	Warm	0.16	0.42	0.19	0.62	0.30	1.07	0.21	0.87	0.12	0.29	0.00	0.00	0.00	0.012
Mesa Verde NP, CO	Cold	0.36	0.34	0.21	0.22	0.15	0.27	0.12	0.19	0.06	0.00	0.00	0.00	0.00	0.011
Mesa Verde NP, CO	Warm	0.46	0.70	0.34	0.45	0.23	0.78	0.15	0.42	0.08	0.12	0.00	0.00	0.00	0.005
Moosehorn NWR, ME	Cold	1.11	1.21	1.02	0.99	0.79	0.97	0.68	0.74	0.53	0.38	0.51	0.45	0.00	0.045
Moosehorn NWR, ME	Warm	0.41	1.01	0.91	1.42	0.91	1.28	0.82	1.03	0.50	0.39	0.53	0.33	0.25	0.009
Mount Ranier NP, WA	Cold	0.48	0.64	0.33	0.35	0.21	0.27	0.13	0.19	0.12	0.00	0.00	0.00	0.00	0.017
Mount Ranier NP, WA	Warm	0.43	0.89	0.43	0.80	0.27	0.55	0.20	0.41	0.00	0.00	0.00	0.00	0.00	0.016
Mount Zirkel Wilderness, CO	Cold	0.46	0.55	0.43	0.42	0.29	0.36	0.24	0.28	0.16	0.15	0.00	0.00	0.00	0.004
Mount Zirkel Wilderness, CO	Warm	0.40	0.73	0.48	0.67	0.35	0.78	0.28	0.49	0.19	0.15	0.13	0.00	0.00	0.003
Okefenokee NWR, GA	Cold	0.29	0.38	0.34	0.39	0.31	0.75	0.24	0.59	0.14	0.22	0.08	0.00	0.00	0.023
Okefenokee NWR, GA	Warm	0.20	0.25	0.23	0.51	0.50	0.98	0.45	0.70	0.30	0.29	0.17	0.09	0.00	0.007
Petrified Forest NP, AZ	Cold	0.40	0.44	0.28	0.28	0.16	0.32	0.13	0.25	0.08	0.08	0.00	0.00	0.00	0.018
Petrified Forest NP, AZ	Warm	0.48	0.67	0.38	0.46	0.22	0.78	0.17	0.47	0.08	0.14	0.00	0.00	0.00	0.007
Pinnacles NM, CA	Cold	0.54	0.85	0.66	0.66	0.47	0.99	0.33	0.62	0.19	0.24	0.11	0.10	0.00	0.006
Pinnacles NM, CA	Warm	0.50	1.03	1.09	1.38	0.78	2.03	0.54	1.04	0.37	0.37	0.25	0.19	0.12	0.004
Point Reyes National Seashore, CA	Cold	0.32	0.52	0.31	0.33	0.21	0.62	0.18	0.36	0.11	0.10	0.00	0.00	0.00	0.007
Point Reyes National Seashore, CA	Warm	0.26	0.66	0.20	0.36	0.15	0.46	0.11	0.38	0.07	0.08	0.00	0.00	0.00	0.002
Quabbin Reservoir, MA	Cold	2.75	2.72	2.19	1.91	1.38	1.52	0.86	0.90	0.48	0.37	0.27	0.17	0.12	0.279
Quabbin Reservoir, MA	Warm	2.03	2.61	1.85	1.97	1.17	1.74	0.69	1.15	0.36	0.39	0.16	0.11	0.08	0.045
Reading, MA	Cold	1.41	1.30	0.82	0.79	0.49	1.13	0.51	0.93	0.34	0.39	0.29	0.00	0.00	0.570
Reading, MA	Warm	0.79	1.45	0.61	1.11	0.51	1.38	0.36	1.21	0.24	0.39	0.00	0.00	0.00	0.090
Redwood NP, CA	Cold	0.19	0.31	0.18	0.15	0.12	0.21	0.09	0.16	0.05	0.00	0.00	0.00	0.00	0.006
Redwood NP, CA	Warm	0.32	0.58	0.32	0.31	0.18	0.33	0.10	0.25	0.06	0.09	0.00	0.00	0.00	0.004

Table A.3. Ambient Concentrations of Selected Fine Particle Chemical Species - Kenmore to Redwood (all values in ng/m³)

Site	Composite Sample	Acphenanthrylene	Pyrene	Retene	Benzo(ghi)fluoranthene	Cyclopenta(cd)pyrene	Benz(a)anthracene	Chrysene/Triphenylene	Benzo(k)fluoranthene	Benzo(b)fluoranthene	Benzo(i)fluoranthene	Benzo(e)pyrene	Benzo(a)pyrene	Perylene	Indeno(cd)pyrene
Kenmore Square, Boston, MA	Cold	0.056	1.380	0.129	0.553	0.051	0.277	0.843	0.547	0.532	0.010	0.527	0.202	0.029	0.370
Kenmore Square, Boston, MA	Warm	0.005	0.129	0.015	0.098	0.008	0.047	0.300	0.131	0.212	0.000	0.161	0.035	0.000	0.034
Lassen Volcanic NP, CA	Cold	0.000	0.007	0.026	0.005	0.001	0.002	0.005	0.005	0.005	0.000	0.009	0.004	0.000	0.006
Lassen Volcanic NP, CA	Warm	0.000	0.005	0.016	0.006	0.000	0.001	0.003	0.005	0.006	0.000	0.010	0.003	0.000	0.007
Lone Peak Wilderness, UT	Cold	0.006	0.056	0.022	0.016	0.005	0.021	0.049	0.071	0.073	0.006	0.066	0.038	0.007	0.054
Lone Peak Wilderness, UT	Warm	0.003	0.028	0.018	0.011	0.003	0.013	0.023	0.039	0.034	0.003	0.042	0.025	0.005	0.038
Lye Brook Wilderness, VT	Cold	0.003	0.033	0.000	0.012	0.002	0.006	0.033	0.043	0.075	0.005	0.050	0.016	0.006	0.031
Lye Brook Wilderness, VT	Warm	0.002	0.011	0.000	0.005	0.001	0.002	0.009	0.008	0.024	0.002	0.017	0.004	0.002	0.009
Mammoth Cave NP, KY	Cold	0.007	0.046	0.021	0.020	0.006	0.018	0.052	0.070	0.101	0.007	0.070	0.039	0.005	0.058
Mammoth Cave NP, KY	Warm	0.000	0.014	0.000	0.005	0.001	0.003	0.010	0.014	0.015	0.000	0.018	0.006	0.001	0.012
Mesa Verde NP, CO	Cold	0.002	0.012	0.024	0.005	0.001	0.004	0.008	0.015	0.009	0.000	0.009	0.000	0.000	0.005
Mesa Verde NP, CO	Warm	0.000	0.007	0.015	0.003	0.000	0.001	0.003	0.006	0.005	0.000	0.007	0.000	0.000	0.000
Moosehorn NWR, ME	Cold	0.006	0.046	0.039	0.028	0.006	0.023	0.090	0.108	0.167	0.007	0.126	0.044	0.005	0.071
Moosehorn NWR, ME	Warm	0.000	0.013	0.010	0.006	0.001	0.002	0.010	0.015	0.029	0.000	0.027	0.005	0.000	0.019
Mount Ranier NP, WA	Cold	0.004	0.028	0.061	0.022	0.006	0.013	0.035	0.092	0.110	0.012	0.093	0.054	0.017	0.095
Mount Ranier NP, WA	Warm	0.002	0.027	0.018	0.019	0.002	0.005	0.020	0.036	0.067	0.010	0.054	0.015	0.020	0.047
Mount Zirkel Wilderness, CO	Cold	0.000	0.006	0.013	0.005	0.000	0.000	0.002	0.005	0.006	0.000	0.011	0.000	0.000	0.005
Mount Zirkel Wilderness, CO	Warm	0.000	0.006	0.007	0.005	0.000	0.000	0.002	0.003	0.003	0.000	0.008	0.000	0.000	0.002
Okefenokee NWR, GA	Cold	0.003	0.024	0.049	0.014	0.003	0.008	0.024	0.033	0.042	0.004	0.036	0.018	0.003	0.035
Okefenokee NWR, GA	Warm	0.000	0.009	0.018	0.003	0.000	0.000	0.004	0.006	0.010	0.000	0.012	0.004	0.000	0.007
Petrified Forest NP, AZ	Cold	0.002	0.020	0.132	0.011	0.002	0.007	0.015	0.024	0.025	0.002	0.022	0.011	0.000	0.015
Petrified Forest NP, AZ	Warm	0.000	0.012	0.056	0.008	0.000	0.003	0.007	0.008	0.010	0.000	0.016	0.004	0.000	0.006
Pinnacles NM, CA	Cold	0.002	0.008	0.025	0.009	0.001	0.007	0.016	0.044	0.058	0.006	0.048	0.029	0.006	0.037
Pinnacles NM, CA	Warm	0.000	0.006	0.014	0.006	0.000	0.002	0.004	0.008	0.012	0.000	0.025	0.003	0.000	0.009
Point Reyes National Seashore, CA	Cold	0.000	0.002	0.052	0.005	0.000	0.002	0.008	0.023	0.023	0.003	0.025	0.007	0.000	0.017
Point Reyes National Seashore, CA	Warm	0.000	0.002	0.026	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.000	0.000	0.000
Quabbin Reservoir, MA	Cold	0.020	0.197	0.087	0.090	0.015	0.064	0.266	0.219	0.292	0.008	0.197	0.083	0.012	0.146
Quabbin Reservoir, MA	Warm	0.004	0.033	0.035	0.000	0.002	0.011	0.042	0.033	0.051	0.000	0.044	0.014	0.000	0.027
Reading, MA	Cold	0.030	0.414	0.136	0.239	0.027	0.123	0.488	0.530	0.517	0.011	0.424	0.139	0.019	0.258
Reading, MA	Warm	0.003	0.051	0.000	0.031	0.003	0.015	0.089	0.072	0.115	0.000	0.120	0.030	0.000	0.060
Redwood NP, CA	Cold	0.000	0.006	0.025	0.005	0.000	0.002	0.008	0.015	0.021	0.004	0.019	0.000	0.000	0.011
Redwood NP, CA	Warm	0.002	0.005	0.015	0.004	0.000	0.002	0.004	0.008	0.011	0.005	0.015	0.004	0.000	0.010

Table A.3. Ambient Concentrations of Selected Fine Particle Chemical Species - Kenmore to Redwood (all values in ng/m³)

Site	Composite Sample	Benzo(ghi)perylene	Indeno(cd)fluoranthene	Dibenz[a,h]anthracene	Coronene	22,29,30-Trisnorhopane	22,29,30-Trisnorhopane	Trisnorhopane	17a(H)-21b(H)-29-Norhopane	18a(H)-29-Norhopane	17b(H)-21a(H)-Normoretane	17a(H)-21b(H)-Hopane	17b(H),21a(H)-Moretane	22S, 17a(H),21b(H)-Homohopane	22R, 17a(H),21b(H)-Homohopane	22S, 17a(H),21b(H)-Bishomohopane
Kenmore Square, Boston, MA	Cold	0.775	0.167	0.041	2.121	0.222	0.169	0.832	0.168	0.000	0.952	0.101	0.397	0.377	0.238	
	Warm	0.254	0.042	0.014	0.819	0.241	0.192	0.825	0.174	0.000	0.874	0.080	0.353	0.307	0.206	
Lassen Volcanic NP, CA	Cold	0.016	0.003	0.000	0.049	0.014	0.013	0.040	0.012	0.000	0.050	0.000	0.019	0.012	0.000	
Lassen Volcanic NP, CA	Warm	0.015	0.003	0.000	0.045	0.012	0.011	0.047	0.014	0.000	0.055	0.000	0.017	0.015	0.009	
Lone Peak Wilderness, UT	Cold	0.078	0.018	0.010	0.165	0.009	0.017	0.049	0.014	0.000	0.065	0.000	0.027	0.018	0.019	
Lone Peak Wilderness, UT	Warm	0.054	0.016	0.007	0.134	0.011	0.000	0.066	0.020	0.000	0.094	0.000	0.042	0.039	0.022	
Lye Brook Wilderness, VT	Cold	0.042	0.011	0.003	0.102	0.018	0.015	0.168	0.031	0.000	0.165	0.000	0.121	0.105	0.089	
Lye Brook Wilderness, VT	Warm	0.014	0.002	0.000	0.042	0.014	0.013	0.065	0.013	0.000	0.076	0.000	0.036	0.027	0.031	
Mammoth Cave NP, KY	Cold	0.080	0.024	0.009	0.197	0.014	0.014	0.099	0.020	0.000	0.122	0.000	0.068	0.056	0.038	
Mammoth Cave NP, KY	Warm	0.014	0.005	0.003	0.036	0.016	0.010	0.056	0.015	0.000	0.079	0.000	0.038	0.035	0.025	
Mesa Verde NP, CO	Cold	0.009	0.003	0.000	0.034	0.016	0.019	0.131	0.022	0.000	0.119	0.011	0.068	0.055	0.041	
Mesa Verde NP, CO	Warm	0.006	0.000	0.000	0.035	0.021	0.023	0.136	0.022	0.000	0.147	0.015	0.080	0.060	0.047	
Moosehorn NWR, ME	Cold	0.094	0.030	0.011	0.157	0.020	0.021	0.121	0.021	0.000	0.125	0.000	0.064	0.056	0.043	
Moosehorn NWR, ME	Warm	0.028	0.008	0.002	0.093	0.012	0.015	0.065	0.024	0.000	0.090	0.000	0.038	0.031	0.029	
Mount Ranier NP, WA	Cold	0.107	0.033	0.010	0.156	0.036	0.041	0.305	0.048	0.000	0.292	0.022	0.207	0.166	0.146	
Mount Ranier NP, WA	Warm	0.070	0.021	0.007	0.155	0.050	0.040	0.450	0.078	0.000	0.439	0.037	0.287	0.247	0.167	
Mount Zirkel Wilderness, CO	Cold	0.009	0.000	0.000	0.046	0.019	0.023	0.147	0.025	0.000	0.201	0.018	0.113	0.109	0.066	
Mount Zirkel Wilderness, CO	Warm	0.009	0.000	0.000	0.029	0.008	0.014	0.053	0.016	0.000	0.081	0.000	0.032	0.020	0.017	
Okefenokee NWR, GA	Cold	0.047	0.016	0.005	0.103	0.011	0.000	0.046	0.011	0.000	0.073	0.000	0.038	0.028	0.020	
Okefenokee NWR, GA	Warm	0.014	0.004	0.000	0.033	0.012	0.007	0.044	0.013	0.000	0.058	0.018	0.030	0.043	0.020	
Petrified Forest NP, AZ	Cold	0.020	0.008	0.002	0.043	0.014	0.020	0.069	0.018	0.000	0.095	0.013	0.037	0.029	0.024	
Petrified Forest NP, AZ	Warm	0.012	0.002	0.000	0.032	0.013	0.011	0.060	0.018	0.000	0.079	0.011	0.034	0.036	0.022	
Pinnacles NM, CA	Cold	0.050	0.017	0.006	0.076	0.006	0.000	0.029	0.009	0.000	0.042	0.000	0.019	0.015	0.000	
Pinnacles NM, CA	Warm	0.017	0.004	0.000	0.046	0.009	0.009	0.044	0.015	0.000	0.066	0.000	0.019	0.015	0.008	
Point Reyes National Seashore, CA	Cold	0.025	0.010	0.000	0.063	0.012	0.016	0.062	0.017	0.000	0.075	0.000	0.034	0.032	0.022	
Point Reyes National Seashore, CA	Warm	0.003	0.000	0.000	0.000	0.012	0.012	0.062	0.012	0.000	0.070	0.000	0.032	0.028	0.017	
Quabbin Reservoir, MA	Cold	0.172	0.061	0.015	0.372	0.037	0.028	0.113	0.025	0.000	0.159	0.000	0.047	0.039	0.028	
Quabbin Reservoir, MA	Warm	0.032	0.010	0.003	0.103	0.027	0.015	0.067	0.016	0.000	0.079	0.000	0.023	0.024	0.000	
Reading, MA	Cold	0.479	0.124	0.028	1.034	0.094	0.080	0.320	0.080	0.000	0.387	0.045	0.163	0.134	0.087	
Reading, MA	Warm	0.145	0.026	0.004	0.441	0.064	0.054	0.240	0.056	0.000	0.266	0.020	0.106	0.098	0.064	
Redwood NP, CA	Cold	0.017	0.005	0.000	0.052	0.010	0.013	0.073	0.014	0.000	0.072	0.000	0.045	0.032	0.025	
Redwood NP, CA	Warm	0.012	0.004	0.000	0.045	0.011	0.011	0.094	0.015	0.000	0.089	0.000	0.049	0.042	0.034	

Table A.3. Ambient Concentrations of Selected Fine Particle Chemical Species - Kenmore to Redwood (all values in ng/m³)

Site	Composite Sample	22R, 17a(H),21b(H)- Bishomohopane	22S, 17a(H),21b(H)- Trishomohopane	22R, 17a(H),21b(H)- Trishomohopane	20R+S, abb-Cholestane	20R, aaa-Cholestane	20R+S, abb-Ergostane	20R+S, abb-Sitostane	1H-Phenalen-1-one	Anthracen-9,10-dione	Benz(de)anthracen-7-one	Benz(a)anthracen-7,12-dione	Dibenzofuran	Squalene	Nonanal
Kenmore Square, Boston, MA	Cold	0.175	0.163	0.097	0.403	0.306	0.269	0.510	0.223	0.893	0.501	0.185	0.02	1.27	0.00
Kenmore Square, Boston, MA	Warm	0.153	0.145	0.090	0.464	0.321	0.265	0.427	0.044	0.366	0.105	0.049	0.04	0.14	2.76
Lassen Volcanic NP, CA	Cold	0.000	0.000	0.000	0.018	0.020	0.000	0.020	0.000	0.000	0.000	0.000	0.00	1.14	0.08
Lassen Volcanic NP, CA	Warm	0.010	0.000	0.000	0.032	0.023	0.000	0.025	0.000	0.000	0.000	0.000	0.00	0.64	0.08
Lone Peak Wilderness, UT	Cold	0.013	0.013	0.000	0.026	0.022	0.000	0.032	0.010	0.036	0.047	0.039	0.00	1.14	0.00
Lone Peak Wilderness, UT	Warm	0.020	0.021	0.000	0.021	0.026	0.000	0.034	0.000	0.000	0.018	0.000	0.00	1.37	0.00
Lye Brook Wilderness, VT	Cold	0.061	0.077	0.051	0.033	0.034	0.000	0.041	0.000	0.015	0.031	0.011	0.00	1.03	0.00
Lye Brook Wilderness, VT	Warm	0.017	0.020	0.013	0.028	0.019	0.000	0.028	0.000	0.000	0.006	0.000	0.00	1.00	0.41
Mammoth Cave NP, KY	Cold	0.037	0.031	0.019	0.031	0.027	0.000	0.040	0.006	0.025	0.085	0.040	0.00	1.35	0.18
Mammoth Cave NP, KY	Warm	0.021	0.021	0.012	0.000	0.000	0.000	0.028	0.000	0.000	0.000	0.000	0.00	0.66	0.00
Mesa Verde NP, CO	Cold	0.036	0.028	0.019	0.042	0.030	0.034	0.047	0.000	0.005	0.010	0.000	0.00	1.00	0.14
Mesa Verde NP, CO	Warm	0.038	0.034	0.021	0.044	0.031	0.035	0.058	0.000	0.000	0.000	0.000	0.00	1.15	0.07
Moosehorn NWR, ME	Cold	0.030	0.031	0.020	0.043	0.036	0.000	0.053	0.015	0.024	0.093	0.037	0.00	0.63	0.12
Moosehorn NWR, ME	Warm	0.023	0.019	0.012	0.020	0.034	0.000	0.037	0.000	0.000	0.000	0.000	0.00	0.98	0.00
Mount Ranier NP, WA	Cold	0.108	0.120	0.073	0.054	0.041	0.000	0.081	0.007	0.009	0.096	0.023	0.00	0.85	0.12
Mount Ranier NP, WA	Warm	0.145	0.139	0.093	0.069	0.046	0.000	0.114	0.000	0.000	0.019	0.000	0.00	0.75	0.22
Mount Zirkel Wilderness, CO	Cold	0.054	0.050	0.029	0.038	0.031	0.052	0.083	0.000	0.000	0.000	0.000	0.00	1.07	0.11
Mount Zirkel Wilderness, CO	Warm	0.017	0.009	0.000	0.021	0.023	0.026	0.034	0.000	0.000	0.000	0.000	0.00	0.72	0.13
Okefenokee NWR, GA	Cold	0.016	0.016	0.008	0.030	0.014	0.000	0.029	0.000	0.012	0.036	0.025	0.00	0.72	0.11
Okefenokee NWR, GA	Warm	0.022	0.030	0.010	0.000	0.000	0.000	0.023	0.000	0.000	0.000	0.000	0.00	0.75	0.00
Petrified Forest NP, AZ	Cold	0.019	0.017	0.012	0.035	0.036	0.041	0.048	0.000	0.000	0.020	0.005	0.00	0.80	0.00
Petrified Forest NP, AZ	Warm	0.020	0.020	0.008	0.036	0.030	0.032	0.036	0.000	0.000	0.000	0.000	0.00	0.59	0.00
Pinnacles NM, CA	Cold	0.000	0.000	0.000	0.000	0.000	0.000	0.018	0.000	0.000	0.049	0.014	0.00	0.91	0.00
Pinnacles NM, CA	Warm	0.008	0.000	0.000	0.000	0.000	0.000	0.028	0.000	0.000	0.000	0.000	0.00	0.79	0.00
Point Reyes National Seashore, CA	Cold	0.018	0.015	0.012	0.021	0.016	0.000	0.034	0.000	0.009	0.026	0.012	0.00	0.61	0.00
Point Reyes National Seashore, CA	Warm	0.015	0.013	0.006	0.028	0.022	0.019	0.027	0.000	0.000	0.000	0.000	0.00	0.69	0.00
Quabbin Reservoir, MA	Cold	0.019	0.000	0.000	0.052	0.035	0.000	0.063	0.000	0.110	0.117	0.036	0.00	0.35	13.12
Quabbin Reservoir, MA	Warm	0.000	0.000	0.000	0.000	0.000	0.000	0.024	0.000	0.052	0.009	0.000	0.00	0.21	5.00
Reading, MA	Cold	0.084	0.055	0.038	0.174	0.140	0.104	0.185	0.108	0.347	0.349	0.111	0.03	0.18	3.68
Reading, MA	Warm	0.048	0.042	0.028	0.092	0.105	0.066	0.132	0.000	0.217	0.031	0.000	0.00	0.28	8.21
Redwood NP, CA	Cold	0.015	0.013	0.000	0.019	0.016	0.000	0.023	0.003	0.000	0.008	0.000	0.00	0.52	0.00
Redwood NP, CA	Warm	0.033	0.020	0.014	0.026	0.015	0.000	0.020	0.000	0.000	0.005	0.000	0.00	0.79	0.00

Table A.3. Ambient Concentrations of Selected Fine Particle Chemical Species - Kenmore to Redwood (all values in ng/m³)

Site	Composite Sample	Levoglucosan	8,15-Pimaradienoic Acid	Pimaric Acid	Sandaracopimaric Acid	Isopimaric Acid	Dehydroabietic Acid	Abietic Acid	Abieta-6,8,11,13,15-pentatrien-18-oic Acid	Abieta-6,8,11,13-tetraen-18-oic Acid	Abieta-8,11,13,15-tetraen-18-oic Acid	7-Oxodehydroabietic Acid	Octanoic Acid	Nonanoic Acid	Decanoic Acid
Kenmore Square, Boston, MA	Cold	90.5	0.00	0.04	0.04	0.29	0.89	0.00	0.14	0.19	0.06	0.20	1.28	3.72	2.06
Kenmore Square, Boston, MA	Warm	23.9	0.00	0.00	0.00	0.00	0.37	0.00	0.00	0.00	0.00	0.15	0.72	1.93	1.30
Lassen Volcanic NP, CA	Cold	10.9	0.06	0.06	0.03	0.17	1.41	0.00	0.02	0.27	0.15	0.20	0.48	0.56	0.99
Lassen Volcanic NP, CA	Warm	17.5	0.07	0.09	0.05	0.37	2.09	0.00	0.02	0.46	0.17	0.28	0.28	0.48	0.75
Lone Peak Wilderness, UT	Cold	19.8	0.18	0.03	0.03	0.14	0.90	0.00	0.03	0.21	0.09	0.16	0.41	0.70	1.08
Lone Peak Wilderness, UT	Warm	23.9	0.51	0.05	0.06	0.35	2.30	0.00	0.04	0.49	0.18	0.33	0.67	0.47	0.80
Lye Brook Wilderness, VT	Cold	10.0	0.02	0.02	0.01	0.07	0.37	0.00	0.03	0.06	0.04	0.07	0.29	0.65	0.73
Lye Brook Wilderness, VT	Warm	12.7	0.00	0.00	0.00	0.13	0.12	0.00	0.01	0.02	0.02	0.05	0.13	0.32	0.52
Mammoth Cave NP, KY	Cold	56.3	0.09	0.03	0.02	0.12	1.66	0.00	0.06	0.19	0.13	0.25	0.20	0.44	0.59
Mammoth Cave NP, KY	Warm	0.0	0.00	0.01	0.00	0.18	0.22	0.00	0.06	0.16	0.05	0.14	0.10	0.47	0.42
Mesa Verde NP, CO	Cold	2.2	0.13	0.02	0.01	0.04	0.40	0.00	0.02	0.08	0.10	0.09	0.17	0.58	0.91
Mesa Verde NP, CO	Warm	1.8	0.10	0.01	0.01	0.07	0.40	0.00	0.02	0.07	0.06	0.10	0.23	0.46	0.82
Moosehorn NWR, ME	Cold	33.4	0.04	0.10	0.09	0.37	2.66	0.00	0.05	0.27	0.21	0.28	0.22	0.48	0.76
Moosehorn NWR, ME	Warm	30.6	0.00	0.00	0.00	0.00	1.64	0.00	0.00	0.30	0.00	0.26	0.00	0.60	0.35
Mount Ranier NP, WA	Cold	161.0	0.20	0.02	0.16	0.95	7.80	0.18	0.07	0.97	0.45	0.76	0.22	0.35	0.59
Mount Ranier NP, WA	Warm	86.9	0.00	0.00	0.00	0.00	2.42	0.00	0.00	0.00	0.00	0.24	0.00	0.00	0.00
Mount Zirkel Wilderness, CO	Cold	2.4	0.03	0.00	0.00	0.03	0.54	0.00	0.00	0.04	0.04	0.04	0.21	0.55	0.87
Mount Zirkel Wilderness, CO	Warm	2.7	0.03	0.01	0.02	0.00	0.22	0.00	0.00	0.03	0.00	0.04	0.00	0.65	0.83
Okefenokee NWR, GA	Cold	53.5	0.08	0.18	0.06	0.36	5.46	0.04	0.36	1.61	1.10	1.74	0.15	0.23	0.41
Okefenokee NWR, GA	Warm	23.2	0.03	0.03	0.00	0.15	1.10	0.00	0.14	0.95	0.28	0.82	0.18	0.18	0.38
Petrified Forest NP, AZ	Cold	13.4	0.78	0.16	0.14	0.26	2.63	0.03	0.05	0.66	0.34	0.38	0.26	0.59	0.84
Petrified Forest NP, AZ	Warm	6.2	0.13	0.08	0.14	0.14	1.61	0.00	0.02	0.38	0.23	0.33	0.28	0.50	0.77
Pinnacles NM, CA	Cold	68.9	0.08	0.21	0.10	0.45	3.95	0.04	0.05	0.89	0.22	0.43	0.33	0.53	0.62
Pinnacles NM, CA	Warm	12.3	0.00	0.05	0.02	0.04	0.99	0.00	0.02	0.14	0.06	0.21	0.24	0.33	0.49
Point Reyes National Seashore, CA	Cold	37.0	0.16	0.21	0.06	0.41	3.09	0.04	0.02	0.39	0.13	0.36	0.17	0.32	0.49
Point Reyes National Seashore, CA	Warm	6.9	0.00	0.00	0.00	0.00	0.17	0.00	0.00	0.01	0.01	0.06	0.40	0.91	0.92
Quabbin Reservoir, MA	Cold	87.6	0.03	0.03	0.04	0.16	0.75	0.05	0.06	0.15	0.07	0.18	0.61	1.51	1.06
Quabbin Reservoir, MA	Warm	15.1	0.00	0.00	0.00	0.00	0.34	0.00	0.05	0.10	0.04	0.11	0.49	1.25	1.03
Reading, MA	Cold	162.2	0.05	0.07	0.05	0.20	1.43	0.07	0.11	0.28	0.11	0.26	0.82	2.27	1.39
Reading, MA	Warm	38.0	0.00	0.01	0.02	0.00	0.36	0.00	0.05	0.07	0.07	0.16	0.62	1.44	0.98
Redwood NP, CA	Cold	17.9	0.04	0.01	0.03	0.19	1.50	0.00	0.02	0.18	0.12	0.34	0.17	0.36	0.57
Redwood NP, CA	Warm	44.5	0.03	0.00	0.04	0.21	1.63	0.02	0.02	0.24	0.13	0.32	0.21	0.47	0.63

Table A.3. Ambient Concentrations of Selected Fine Particle Chemical Species - Kenmore to Redwood (all values in ng/m³)

Site	Composite Sample	Undecanoic Acid	Dodecanoic Acid	Tridecanoic Acid	Tetradecanoic Acid	Pentadecanoic Acid	Hexadecanoic Acid	Heptadecanoic Acid	Octadecanoic Acid	Nonadecanoic Acid	Eicosanoic Acid	Heneicosanoic Acid	Docosanoic Acid	Tricosanoic Acid	Tetracosanoic Acid
Kenmore Square, Boston, MA	Cold	0.90	4.12	1.25	3.70	1.96	27.07	1.32	13.88	0.38	1.46	0.71	3.23	0.99	4.24
Kenmore Square, Boston, MA	Warm	0.46	4.11	1.49	4.58	1.78	21.93	1.12	11.64	0.39	2.29	0.51	2.91	0.80	2.63
Lassen Volcanic NP, CA	Cold	0.14	1.86	0.30	2.78	1.28	7.34	0.45	5.12	0.11	0.58	0.17	1.68	0.37	1.70
Lassen Volcanic NP, CA	Warm	0.16	1.57	0.31	2.57	1.41	9.40	0.54	4.47	0.17	0.82	0.25	2.07	0.46	2.11
Lone Peak Wilderness, UT	Cold	0.16	1.68	0.28	2.23	0.98	6.27	0.34	3.76	0.09	0.42	0.16	1.08	0.30	1.18
Lone Peak Wilderness, UT	Warm	0.13	1.30	0.22	2.02	0.82	6.95	0.41	4.50	0.18	1.10	0.39	3.13	0.78	3.36
Lye Brook Wilderness, VT	Cold	0.12	1.31	0.21	1.45	0.70	4.52	0.26	2.92	0.08	0.37	0.18	0.90	0.28	1.06
Lye Brook Wilderness, VT	Warm	0.09	1.14	0.23	1.65	0.83	7.20	0.40	3.72	0.17	1.41	0.28	1.86	0.51	1.68
Mammoth Cave NP, KY	Cold	0.11	1.28	0.21	1.74	0.87	7.67	0.45	4.47	0.21	0.83	0.53	2.48	1.04	4.10
Mammoth Cave NP, KY	Warm	0.07	1.06	0.21	1.52	0.87	8.74	0.51	5.02	0.21	2.05	0.45	2.90	0.90	3.16
Mesa Verde NP, CO	Cold	0.17	1.95	0.28	1.84	0.80	4.60	0.25	3.08	0.05	0.28	0.08	0.61	0.15	0.65
Mesa Verde NP, CO	Warm	0.15	1.71	0.31	2.27	1.14	7.23	0.41	3.63	0.11	0.47	0.16	1.17	0.30	1.40
Moosehorn NWR, ME	Cold	0.17	1.84	0.36	2.53	1.05	11.48	0.63	7.99	0.34	1.29	0.59	2.59	0.66	2.28
Moosehorn NWR, ME	Warm	0.00	1.05	0.00	2.21	0.44	13.11	0.55	8.56	0.24	2.58	0.00	2.78	0.24	1.63
Mount Ranier NP, WA	Cold	0.10	1.35	0.24	2.06	1.09	7.69	0.43	4.25	0.24	1.69	0.41	5.03	0.75	5.47
Mount Ranier NP, WA	Warm	0.00	0.00	0.00	2.47	1.22	17.21	0.44	7.65	0.00	0.86	0.00	1.86	0.00	2.06
Mount Zirkel Wilderness, CO	Cold	0.14	1.39	0.27	1.86	0.75	5.26	0.30	3.30	0.06	0.23	0.07	0.41	0.13	0.47
Mount Zirkel Wilderness, CO	Warm	0.16	1.32	0.27	2.25	1.18	7.68	0.39	4.24	0.08	0.32	0.00	0.55	0.16	0.60
Okefenokee NWR, GA	Cold	0.08	1.13	0.15	1.42	0.68	6.14	0.33	3.87	0.15	0.88	0.37	2.00	0.89	4.25
Okefenokee NWR, GA	Warm	0.05	0.94	0.20	1.41	0.64	5.77	0.33	3.93	0.14	0.84	0.30	1.76	0.66	3.21
Petrified Forest NP, AZ	Cold	0.14	1.57	0.27	1.92	1.06	5.94	0.35	3.28	0.07	0.50	0.12	1.07	0.25	1.07
Petrified Forest NP, AZ	Warm	0.16	1.35	0.29	2.37	1.60	8.37	0.43	3.43	0.12	0.60	0.19	1.50	0.40	1.71
Pinnacles NM, CA	Cold	0.12	1.22	0.24	1.85	0.91	8.72	0.49	4.86	0.17	0.97	0.38	3.10	0.76	4.00
Pinnacles NM, CA	Warm	0.13	1.25	0.28	1.97	1.00	9.58	0.58	5.68	0.23	0.95	0.38	2.20	0.61	2.46
Point Reyes National Seashore, CA	Cold	0.10	1.30	0.23	1.92	0.97	7.64	0.37	4.30	0.11	0.73	0.24	2.15	0.45	2.41
Point Reyes National Seashore, CA	Warm	0.14	1.50	0.28	2.92	1.30	8.89	0.38	3.90	0.11	0.66	0.14	1.04	0.23	1.08
Quabbin Reservoir, MA	Cold	0.30	1.78	0.37	1.18	0.87	6.93	0.49	4.00	0.25	1.02	0.62	2.80	0.83	3.71
Quabbin Reservoir, MA	Warm	0.24	2.18	0.59	1.94	0.94	6.79	0.43	3.08	0.31	1.89	0.42	2.44	0.65	2.34
Reading, MA	Cold	0.54	2.81	0.85	2.09	1.13	18.62	0.90	10.05	0.41	1.51	0.90	4.11	1.23	5.63
Reading, MA	Warm	0.30	2.89	0.98	2.31	1.20	13.36	0.75	7.87	0.38	2.30	0.56	3.14	0.90	3.01
Redwood NP, CA	Cold	0.09	0.92	0.14	1.22	0.65	5.19	0.28	2.71	0.09	0.59	0.21	2.36	0.41	3.45
Redwood NP, CA	Warm	0.11	1.07	0.21	1.90	1.10	7.85	0.38	3.17	0.16	1.11	0.32	3.64	0.59	4.77

Table A.3. Ambient Concentrations of Selected Fine Particle Chemical Species - Kenmore to Redwood (all values in ng/m³)

Site	Composite Sample	Pentacosanoic Acid	Hexacosanoic Acid	Heptacosanoic Acid	Octacosanoic Acid	Nonacosanoic Acid	Triacontanoic Acid	Hentriacontanoic Acid	Dotriacontanoic Acid	9-Hexadecenoic Acid	9,12-Octadecanedienoic Acid	9-Octadecenoic Acid	Propanedioic Acid	Methylpropanedioic Acid	Butanedioic Acid
Kenmore Square, Boston, MA	Cold	0.49	1.73	0.17	0.61	0.09	0.35	0.02	0.16	0.45	0.82	2.86	5.20	0.00	20.16
Kenmore Square, Boston, MA	Warm	0.45	1.44	0.24	1.20	0.17	0.73	0.07	0.26	0.00	0.00	0.60	10.39	0.85	23.96
Lassen Volcanic NP, CA	Cold	0.17	0.56	0.07	0.31	0.06	0.31	0.03	0.15	2.34	0.66	1.62	0.00	0.00	2.36
Lassen Volcanic NP, CA	Warm	0.22	0.76	0.12	0.50	0.09	0.44	0.03	0.16	1.91	0.57	1.59	1.00	0.00	8.03
Lone Peak Wilderness, UT	Cold	0.16	0.54	0.06	0.24	0.04	0.14	0.01	0.04	2.36	0.33	1.57	0.29	0.00	5.22
Lone Peak Wilderness, UT	Warm	0.38	1.55	0.16	0.96	0.11	0.62	0.03	0.12	1.71	0.67	1.75	0.30	0.00	5.75
Lye Brook Wilderness, VT	Cold	0.15	0.49	0.06	0.26	0.04	0.18	0.02	0.07	1.44	0.32	1.18	0.78	0.00	5.38
Lye Brook Wilderness, VT	Warm	0.28	0.94	0.17	0.86	0.11	0.54	0.05	0.17	1.62	0.43	1.51	8.75	0.58	16.16
Mammoth Cave NP, KY	Cold	0.53	2.23	0.24	1.17	0.20	1.00	0.10	0.48	1.97	0.62	1.75	1.00	0.15	6.78
Mammoth Cave NP, KY	Warm	0.53	1.81	0.35	1.73	0.25	1.45	0.12	0.55	1.35	1.54	1.78	19.71	1.45	26.93
Mesa Verde NP, CO	Cold	0.09	0.26	0.05	0.18	0.03	0.12	0.00	0.04	1.66	0.19	1.21	0.00	0.00	1.74
Mesa Verde NP, CO	Warm	0.17	0.55	0.10	0.55	0.08	0.45	0.03	0.12	1.94	0.23	1.41	0.67	0.00	4.46
Moosehorn NWR, ME	Cold	0.30	0.84	0.13	0.43	0.08	0.25	0.03	0.11	1.38	0.34	1.28	0.56	0.00	4.99
Moosehorn NWR, ME	Warm	0.00	0.44	0.00	0.00	0.00	0.00	0.00	0.00	1.17	0.49	0.64	12.02	0.00	10.34
Mount Ranier NP, WA	Cold	0.30	1.22	0.07	0.30	0.04	0.41	0.02	0.14	1.91	2.45	1.37	0.18	0.00	3.48
Mount Ranier NP, WA	Warm	0.52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.30	0.00	0.00	2.82	0.00	6.44
Mount Zirkel Wilderness, CO	Cold	0.08	0.21	0.03	0.15	0.02	0.10	0.01	0.03	1.50	0.25	1.19	0.00	0.00	0.79
Mount Zirkel Wilderness, CO	Warm	0.06	0.21	0.00	0.16	0.00	0.00	0.00	0.00	1.37	0.29	0.97	0.59	0.00	3.04
Okefenokee NWR, GA	Cold	0.44	2.63	0.20	0.93	0.17	0.77	0.09	0.34	1.54	0.85	1.29	4.36	0.27	10.28
Okefenokee NWR, GA	Warm	0.54	2.68	0.36	1.79	0.27	1.05	0.12	0.39	1.46	1.47	1.86	4.28	0.33	10.77
Petrified Forest NP, AZ	Cold	0.12	0.34	0.06	0.25	0.04	0.18	0.01	0.06	1.60	0.21	1.38	0.18	0.00	2.50
Petrified Forest NP, AZ	Warm	0.20	0.63	0.12	0.62	0.09	0.54	0.03	0.13	1.51	0.23	1.22	0.41	0.00	4.94
Pinnacles NM, CA	Cold	0.40	1.94	0.14	0.60	0.10	0.42	0.05	0.16	1.47	0.62	1.37	0.57	0.00	9.87
Pinnacles NM, CA	Warm	0.35	1.13	0.21	0.87	0.17	0.78	0.07	0.23	1.93	0.29	1.52	2.19	0.30	12.69
Point Reyes National Seashore, CA	Cold	0.24	1.13	0.10	0.46	0.07	0.28	0.03	0.11	1.88	0.43	1.49	0.35	0.00	13.57
Point Reyes National Seashore, CA	Warm	0.17	1.02	0.11	1.20	0.05	0.29	0.01	0.08	2.18	0.29	1.54	0.00	0.00	2.84
Quabbin Reservoir, MA	Cold	0.39	1.54	0.14	0.58	0.07	0.29	0.03	0.12	0.00	0.17	0.71	6.01	0.00	16.40
Quabbin Reservoir, MA	Warm	0.38	1.33	0.24	1.13	0.14	0.63	0.05	0.21	0.00	0.00	0.47	14.11	0.88	21.70
Reading, MA	Cold	0.59	2.24	0.17	0.67	0.09	0.37	0.03	0.16	0.00	0.66	1.76	3.51	0.00	16.26
Reading, MA	Warm	0.50	1.62	0.28	1.31	0.17	0.79	0.07	0.27	0.00	0.38	1.39	11.94	0.00	24.77
Redwood NP, CA	Cold	0.22	1.25	0.08	0.39	0.07	0.33	0.03	0.14	1.23	1.92	1.22	0.07	0.00	1.97
Redwood NP, CA	Warm	0.27	1.45	0.11	0.52	0.09	0.41	0.04	0.17	2.22	0.99	1.57	0.00	0.00	5.01

Table A.3. Ambient Concentrations of Selected Fine Particle Chemical Species - Kenmore to Redwood (all values in ng/m³)

Site	Composite Sample	Methylbutanedioic Acid	Pentanedioic Acid	Hexanedioic Acid	Heptanedioic Acid	Octanedioic Acid	Nonanedioic Acid
Kenmore Square, Boston, MA	Cold	4.47	9.86	6.27	13.97	2.23	12.42
Kenmore Square, Boston, MA	Warm	2.67	9.61	7.28	6.09	2.15	10.39
Lassen Volcanic NP, CA	Cold	0.48	0.77	1.44	0.32	0.94	2.00
Lassen Volcanic NP, CA	Warm	0.86	2.31	1.91	0.92	1.73	2.76
Lone Peak Wilderness, UT	Cold	0.91	1.72	1.96	0.65	0.61	1.43
Lone Peak Wilderness, UT	Warm	0.84	1.75	1.54	0.53	0.90	2.44
Lye Brook Wilderness, VT	Cold	0.91	1.86	2.11	0.49	0.60	1.20
Lye Brook Wilderness, VT	Warm	1.19	4.13	5.92	1.05	1.80	3.50
Mammoth Cave NP, KY	Cold	1.19	2.02	1.85	0.68	1.27	3.28
Mammoth Cave NP, KY	Warm	1.51	5.67	8.19	1.41	1.45	4.11
Mesa Verde NP, CO	Cold	0.23	0.62	0.95	0.16	0.49	0.76
Mesa Verde NP, CO	Warm	0.45	1.34	1.22	0.57	1.05	1.66
Moosehorn NWR, ME	Cold	0.96	1.77	4.64	0.61	1.22	5.10
Moosehorn NWR, ME	Warm	0.87	0.00	2.00	0.00	0.00	0.00
Mount Ranier NP, WA	Cold	1.28	1.17	1.19	0.35	1.04	2.94
Mount Ranier NP, WA	Warm	1.54	0.00	0.00	0.00	0.00	0.00
Mount Zirkel Wilderness, CO	Cold	0.13	0.28	0.67	0.10	0.32	0.76
Mount Zirkel Wilderness, CO	Warm	0.00	0.51	0.55	0.00	0.55	0.79
Okefenokee NWR, GA	Cold	1.18	2.56	2.47	1.00	1.91	3.72
Okefenokee NWR, GA	Warm	0.67	1.95	4.23	0.43	0.76	3.15
Petrified Forest NP, AZ	Cold	0.42	0.76	1.42	0.23	0.61	1.17
Petrified Forest NP, AZ	Warm	0.55	1.39	1.39	0.58	1.09	1.98
Pinnacles NM, CA	Cold	1.92	2.97	2.09	0.57	1.22	3.35
Pinnacles NM, CA	Warm	1.55	3.55	2.11	0.78	1.48	3.33
Point Reyes National Seashore, CA	Cold	2.07	3.94	2.02	0.91	1.06	2.26
Point Reyes National Seashore, CA	Warm	0.49	1.30	1.02	0.34	0.53	0.95
Quabbin Reservoir, MA	Cold	3.48	7.44	3.19	1.76	1.30	3.38
Quabbin Reservoir, MA	Warm	1.79	7.86	4.68	3.22	2.02	4.58
Reading, MA	Cold	4.37	9.36	5.59	10.05	2.13	11.37
Reading, MA	Warm	2.85	9.21	4.83	3.33	3.36	11.16
Redwood NP, CA	Cold	0.52	0.70	1.03	0.20	0.60	1.39
Redwood NP, CA	Warm	0.87	1.61	1.46	0.47	1.04	2.23

Table A.4. Ambient Concentrations of Selected Fine Particle Chemical Species - Rochester to Yosemite (all values in ng/m³)

Site	Composite Sample	Total Carbon	Silicon	Aluminum	Potassium	Guaiacyl Acetone	Acetovanillone	Vanillin	Syringaldehyde	Homovanillic Acid	Vanillic Acid	Sinapyl Aldehyde	Syringic Acid	Syringyl Acetone	Propionyl Syringol
Rochester, NY	Cold	3651	119	41	0	0.00	0.00	2.49	0.00	0.00	0.00	0.00	2.13	0.00	0.00
Rochester, NY	Warm	4217	146	51	0	0.00	0.00	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Rocky Mountain NP, CO	Cold	443	76	37	5	0.00	0.00	0.06	0.09	0.00	0.06	0.00	0.00	0.00	0.02
Rocky Mountain NP, CO	Warm	942	178	72	13	0.04	0.01	0.11	0.06	0.00	0.00	0.00	0.00	0.02	0.03
San Geronio Wilderness, CA	Cold	1093	116	61	6	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.02
San Geronio Wilderness, CA	Warm	1869	206	101	16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sequoia NP, CA	Cold	2327	72	22	33	1.56	1.27	0.36	0.00	16.79	34.00	0.00	34.38	0.07	1.99
Sequoia NP, CA	Warm	3880	336	161	32	0.42	0.14	0.15	0.00	0.63	0.00	0.00	0.00	0.04	0.02
Sequoia NP, CA	11/11/95	19754	189	135	212	0.00	0.00	0.00	24.62	9.91	0.00	0.00	0.00	24.80	5.42
Sequoia NP, CA	11/29/95	31555	282	166	104	0.00	0.00	0.00	13.23	42.47	0.00	0.00	0.00	12.61	2.67
Shenandoah NP, VA	Cold	1294	65	31	16	0.05	0.01	0.07	0.34	0.00	0.00	0.00	0.00	0.14	0.20
Shenandoah NP, VA	Warm	2732	117	44	23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.07	0.07	0.08
Shining Rock Wilderness, NC	Cold	1235	89	44	22	0.00	0.00	0.05	0.17	0.00	0.00	0.00	0.00	0.09	0.07
Shining Rock Wilderness, NC	Warm	2051	170	80	29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Sipsy Wilderness, AL	Cold	2213	99	45	39	0.09	0.02	0.10	0.15	0.00	0.00	0.00	0.00	0.18	0.12
Sipsy Wilderness, AL	Warm	2562	137	53	41	0.04	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.05	0.00
Snoqualmie National Forest, WA	Cold	661	32	12	9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Snoqualmie National Forest, WA	Warm	795	57	24	22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
South Lake Tahoe, CA	Cold	4324	215	94	17	2.10	0.53	2.74	0.69	24.00	16.31	0.00	5.19	0.53	0.97
South Lake Tahoe, CA	Warm	2176	222	102	7	0.31	0.16	0.67	0.13	1.24	2.62	0.00	0.00	0.10	0.10
Three Sisters Wilderness, OR	Cold	568	31	13	8	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Three Sisters Wilderness, OR	Warm	1529	82	36	31	0.00	0.02	0.12	0.00	0.00	0.00	0.00	0.00	0.05	0.01
Tonto NM, AZ	Cold	1170	134	52	12	0.04	0.01	0.10	0.08	0.00	0.00	0.00	0.00	0.00	0.01
Tonto NM, AZ	Warm	1427	250	77	38	0.04	0.02	0.10	0.03	0.00	0.00	0.00	0.00	0.03	0.01
Upper Buffalo Wilderness, AK	Cold	1585	87	33	28	0.08	0.01	0.10	0.16	0.00	0.00	0.00	0.68	0.03	0.32
Upper Buffalo Wilderness, AK	Warm	2658	282	91	42	0.03	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.03	0.02
Washington, DC	Cold	3313	87	45	7	0.04	0.02	0.29	0.27	0.00	0.00	0.00	2.68	0.05	0.75
Washington, DC	Warm	3783	125	42	11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.01
Weminuche Wilderness, CO	Cold	475	99	35	5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Weminuche Wilderness, CO	Warm	781	152	55	14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Yellowstone NP, CA	Cold	607	66	20	6	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00
Yellowstone NP, CA	Warm	1056	226	72	19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Yosemite NP, CA	Cold	969	65	27	12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Yosemite NP, CA	Warm	1955	178	76	18	0.11	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Yosemite NP, CA	10/25/95	30396	455	270	225	8.77	2.71	10.01	32.79	77.35	0.00	0.00	0.00	26.04	10.45

Table A.4. Ambient Concentrations of Selected Fine Particle Chemical Species - Rochester to Yosemite (all values in ng/m³)

Site	Composite Sample	Acetosyringone	Acetonylsyringol	Juvabione	Dehydrojuvabione	Beta-Sitosterol	Stigmast-4-en-3-one	Stigmasta-3,5-dien-7-one	Stigmasta-4,6-dien-3-one	Stigmastan-3-ol	Stigmastan-3-one	Friedelin	Beta-Amyrone	Beta-Amyrin	Alpha-Amyrone
Rochester, NY	Cold	0.33	0.00	0.00	0.00	0.42	0.17	0.06	0.04	0.10	0.00	0.30	0.02	0.03	0.02
Rochester, NY	Warm	0.00	0.00	0.00	0.00	0.16	0.10	0.06	0.00	0.00	0.00	0.24	0.00	0.01	0.01
Rocky Mountain NP, CO	Cold	0.07	0.00	0.00	0.00	0.08	0.04	0.02	0.00	0.00	0.02	0.03	0.00	0.00	0.02
Rocky Mountain NP, CO	Warm	0.08	0.03	0.00	0.00	0.13	0.08	0.06	0.02	0.05	0.03	0.00	0.01	0.00	0.02
San Geronio Wilderness, CA	Cold	0.07	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
San Geronio Wilderness, CA	Warm	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sequoia NP, CA	Cold	8.55	0.00	0.00	0.00	16.23	3.54	6.99	1.94	1.28	0.00	2.69	0.62	1.13	0.86
Sequoia NP, CA	Warm	0.00	0.00	0.00	0.00	0.65	0.91	0.63	0.23	0.17	0.06	0.17	0.01	0.01	0.03
Sequoia NP, CA	11/11/95	24.07	30.55	2.41	0.00	52.57	19.84	9.97	3.13	5.05	5.31	7.00	3.81	4.77	7.31
Sequoia NP, CA	11/29/95	10.19	16.12	1.66	0.00	43.08	21.30	11.18	4.15	4.86	4.71	9.21	1.42	2.57	3.19
Shenandoah NP, VA	Cold	0.44	0.17	0.00	0.00	0.19	0.12	0.04	0.03	0.06	0.02	0.30	0.01	0.02	0.03
Shenandoah NP, VA	Warm	0.18	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Shining Rock Wilderness, NC	Cold	0.16	0.16	0.00	0.00	0.13	0.11	0.02	0.02	0.00	0.03	0.29	0.01	0.01	0.02
Shining Rock Wilderness, NC	Warm	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sipsy Wilderness, AL	Cold	0.23	0.23	0.00	0.00	0.25	0.44	0.15	0.07	0.00	0.06	0.99	0.03	0.05	0.06
Sipsy Wilderness, AL	Warm	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Snoqualmie National Forest, WA	Cold	0.00	0.03	0.00	0.00	0.09	0.09	0.03	0.02	0.00	0.03	0.07	0.00	0.00	0.01
Snoqualmie National Forest, WA	Warm	0.00	0.00	0.00	0.00	0.11	0.06	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.00
South Lake Tahoe, CA	Cold	2.30	0.57	0.19	0.00	3.99	1.18	1.38	0.28	1.06	0.26	0.39	0.01	0.04	0.02
South Lake Tahoe, CA	Warm	0.20	0.11	0.00	0.00	0.58	0.32	0.24	0.05	0.18	0.11	0.17	0.00	0.01	0.01
Three Sisters Wilderness, OR	Cold	0.00	0.00	0.00	0.00	0.07	0.05	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.00
Three Sisters Wilderness, OR	Warm	0.00	0.05	0.05	0.00	0.14	0.16	0.06	0.02	0.04	0.02	0.05	0.00	0.01	0.01
Tonto NM, AZ	Cold	0.03	0.00	0.00	0.00	0.10	0.09	0.03	0.02	0.00	0.02	0.06	0.00	0.00	0.01
Tonto NM, AZ	Warm	0.04	0.00	0.00	0.00	0.12	0.11	0.04	0.02	0.00	0.03	0.07	0.00	0.01	0.01
Upper Buffalo Wilderness, AK	Cold	0.77	0.00	0.00	0.00	0.24	0.19	0.07	0.04	0.05	0.00	0.55	0.02	0.03	0.03
Upper Buffalo Wilderness, AK	Warm	0.07	0.04	0.05	0.00	0.00	0.38	0.34	0.00	0.00	0.00	1.85	0.04	0.00	0.13
Washington, DC	Cold	1.52	0.06	0.05	0.00	0.55	0.31	0.14	0.07	0.12	0.05	0.82	0.02	0.03	0.03
Washington, DC	Warm	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Weminuche Wilderness, CO	Cold	0.03	0.00	0.00	0.00	0.00	0.03	0.02	0.00	0.00	0.01	0.04	0.00	0.00	0.01
Weminuche Wilderness, CO	Warm	0.00	0.00	0.06	0.00	0.06	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Yellowstone NP, CA	Cold	0.00	0.00	0.05	0.00	0.21	0.10	0.10	0.02	0.06	0.06	0.00	0.00	0.00	0.00
Yellowstone NP, CA	Warm	0.00	0.00	0.00	0.00	0.10	0.05	0.03	0.00	0.03	0.02	0.00	0.00	0.00	0.00
Yosemite NP, CA	Cold	0.03	0.00	0.00	0.00	0.26	0.15	0.07	0.04	0.00	0.03	0.00	0.00	0.00	0.00
Yosemite NP, CA	Warm	0.00	0.00	0.00	0.00	0.47	0.36	0.15	0.08	0.09	0.07	0.12	0.01	0.01	0.02
Yosemite NP, CA	10/25/95	38.89	31.58	2.77	0.00	71.84	24.14	13.99	4.28	7.29	5.96	114.06	6.41	16.49	10.27

Table A.4. Ambient Concentrations of Selected Fine Particle Chemical Species - Rochester to Yosemite (all values in ng/m³)

Site	Composite Sample	Alpha-Amyrin	Alpha-Tocopherol	Delta-Tocopherol	Beta-Tocopherol	Betulin	Cholesterol	Hexadecane	Heptadecane	Octadecane	Nonadecane	Eicosane	Heneicosane	Docosane	Tricosane
Rochester, NY	Cold	0.02	0.00	0.00	0.00	0.00	0.76	0.00	0.16	0.60	1.05	1.31	1.46	1.63	1.66
Rochester, NY	Warm	0.01	0.00	0.00	0.00	0.00	0.57	0.00	0.00	0.00	0.39	0.49	0.93	0.89	1.68
Rocky Mountain NP, CO	Cold	0.01	0.00	0.00	0.00	0.00	0.14	0.00	0.00	0.00	0.00	0.10	0.17	0.25	0.44
Rocky Mountain NP, CO	Warm	0.02	0.00	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.08	0.10	0.19	0.42
San Geronio Wilderness, CA	Cold	0.00	0.00	0.00	0.00	0.00	0.20	0.00	0.00	0.00	0.00	0.08	0.13	0.17	0.29
San Geronio Wilderness, CA	Warm	0.00	0.00	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.06	0.09	0.12	0.32
Sequoia NP, CA	Cold	1.03	2.96	0.25	0.27	0.00	0.33	0.00	0.00	0.00	0.00	0.16	0.38	0.96	2.33
Sequoia NP, CA	Warm	0.04	0.11	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.10	0.15	0.20	0.43
Sequoia NP, CA	11/11/95	0.00	7.95	1.17	2.93	0.00	7.27	0.00	0.00	0.00	0.00	0.93	2.19	3.56	6.35
Sequoia NP, CA	11/29/95	2.90	4.03	0.00	1.24	0.00	2.82	0.00	0.00	0.00	0.00	0.52	1.35	2.78	6.85
Shenandoah NP, VA	Cold	0.03	0.00	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.12	0.17	0.25	0.39
Shenandoah NP, VA	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.14	0.37
Shining Rock Wilderness, NC	Cold	0.02	0.00	0.00	0.00	0.00	0.14	0.00	0.00	0.00	0.00	0.10	0.12	0.13	0.22
Shining Rock Wilderness, NC	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.12	0.23
Sipsy Wilderness, AL	Cold	0.07	0.04	0.00	0.00	0.00	0.19	0.00	0.00	0.00	0.00	0.07	0.11	0.18	0.47
Sipsy Wilderness, AL	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.06	0.10	0.21
Snoqualmie National Forest, WA	Cold	0.01	0.00	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.00	0.10	0.16	0.21	0.29
Snoqualmie National Forest, WA	Warm	0.00	0.00	0.00	0.00	0.00	0.26	0.00	0.00	0.00	0.00	0.08	0.13	0.18	0.31
South Lake Tahoe, CA	Cold	0.03	0.17	0.00	0.00	0.00	0.34	0.00	0.00	0.00	0.00	0.24	0.61	1.16	1.92
South Lake Tahoe, CA	Warm	0.02	0.00	0.00	0.00	0.00	0.29	0.00	0.00	0.00	0.00	0.26	0.40	0.53	1.02
Three Sisters Wilderness, OR	Cold	0.00	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.00	0.08	0.14	0.20	0.31
Three Sisters Wilderness, OR	Warm	0.01	0.00	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.06	0.09	0.14	0.30
Tonto NM, AZ	Cold	0.01	0.00	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.00	0.09	0.15	0.18	0.29
Tonto NM, AZ	Warm	0.01	0.00	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.09	0.12	0.14	0.29
Upper Buffalo Wilderness, AK	Cold	0.04	0.02	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.07	0.14	0.21	0.38
Upper Buffalo Wilderness, AK	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.08	0.13	0.30
Washington, DC	Cold	0.04	0.05	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.11	0.25	0.48	0.86
Washington, DC	Warm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.07	0.14	0.29
Weminuche Wilderness, CO	Cold	0.00	0.00	0.00	0.00	0.00	0.19	0.00	0.00	0.00	0.00	0.11	0.19	0.23	0.39
Weminuche Wilderness, CO	Warm	0.01	0.00	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.10	0.19	0.26	1.35
Yellowstone NP, CA	Cold	0.00	0.00	0.00	0.00	0.00	0.19	0.00	0.00	0.00	0.00	0.10	0.13	0.22	0.32
Yellowstone NP, CA	Warm	0.01	0.00	0.00	0.00	0.00	0.14	0.00	0.00	0.00	0.00	0.09	0.16	0.23	0.36
Yosemite NP, CA	Cold	0.00	0.00	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.11	0.18	0.25	0.39
Yosemite NP, CA	Warm	0.01	0.04	0.00	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.08	0.16	0.20	0.50
Yosemite NP, CA	10/25/95	10.61	9.00	0.00	3.12	0.00	3.42	0.00	1.36	1.22	1.01	1.58	6.16	13.23	22.93

Table A.4. Ambient Concentrations of Selected Fine Particle Chemical Species - Rochester to Yosemite (all values in ng/m³)

Site	Composite Sample	Tetracosane	Pentacosane	Hexacosane	Heptacosane	Octacosane	Nonacosane	Triacosane	Hentriacontane	Dotriacontane	Tritriacontane	Tetratriacontane	Pentatriacontane	Hexatriacontane	Fluoranthene
Rochester, NY	Cold	2.10	2.95	3.60	4.00	3.67	3.82	2.43	2.55	1.27	0.94	0.69	0.41	0.22	0.636
Rochester, NY	Warm	1.35	2.39	2.36	3.06	2.34	3.03	1.67	2.32	0.86	0.81	0.39	0.23	0.13	0.289
Rocky Mountain NP, CO	Cold	0.47	0.47	0.26	0.24	0.13	0.23	0.09	0.15	0.05	0.06	0.00	0.00	0.00	0.006
Rocky Mountain NP, CO	Warm	0.43	0.57	0.24	0.41	0.14	0.78	0.11	0.56	0.05	0.11	0.00	0.00	0.00	0.005
San Geronio Wilderness, CA	Cold	0.32	0.30	0.22	0.26	0.16	0.39	0.12	0.24	0.07	0.08	0.00	0.00	0.00	0.008
San Geronio Wilderness, CA	Warm	0.32	0.64	0.40	0.67	0.30	1.02	0.20	0.57	0.11	0.17	0.05	0.00	0.00	0.006
Sequoia NP, CA	Cold	2.08	0.00	1.55	4.18	1.50	7.46	0.97	5.18	0.40	3.11	0.00	0.71	0.00	0.051
Sequoia NP, CA	Warm	0.44	1.37	0.53	1.34	0.58	2.63	0.38	1.46	0.25	0.45	0.00	0.00	0.00	0.006
Sequoia NP, CA	11/11/95	5.81	14.59	6.92	34.29	6.99	61.00	4.35	49.11	2.10	28.85	0.00	0.00	0.00	0.140
Sequoia NP, CA	11/29/95	10.64	20.56	7.26	32.67	6.45	44.60	3.94	23.64	1.27	14.50	0.00	3.16	0.00	0.259
Shenandoah NP, VA	Cold	0.42	0.48	0.31	0.42	0.20	0.56	0.15	0.37	0.08	0.09	0.00	0.00	0.00	0.046
Shenandoah NP, VA	Warm	0.29	0.72	0.43	0.77	0.27	0.91	0.22	0.70	0.12	0.23	0.06	0.00	0.00	0.015
Shining Rock Wilderness, NC	Cold	0.31	0.47	0.45	0.53	0.35	0.65	0.28	0.51	0.19	0.19	0.09	0.00	0.00	0.018
Shining Rock Wilderness, NC	Warm	0.26	0.45	0.40	0.64	0.32	0.77	0.29	0.63	0.17	0.21	0.11	0.00	0.00	0.010
Sipsy Wilderness, AL	Cold	0.54	0.87	0.94	1.21	1.12	1.94	1.18	1.62	0.65	0.68	0.53	0.38	0.18	0.058
Sipsy Wilderness, AL	Warm	0.30	0.47	0.50	0.83	0.60	1.38	0.67	1.15	0.48	0.52	0.33	0.23	0.00	0.017
Snoqualmie National Forest, WA	Cold	0.29	0.29	0.18	0.17	0.11	0.18	0.08	0.12	0.05	0.00	0.00	0.00	0.00	0.014
Snoqualmie National Forest, WA	Warm	0.40	0.49	0.33	0.35	0.18	0.26	0.13	0.24	0.08	0.07	0.00	0.00	0.00	0.006
South Lake Tahoe, CA	Cold	1.88	2.33	1.32	1.71	0.73	1.18	0.62	0.88	0.37	0.39	0.00	0.00	0.00	0.191
South Lake Tahoe, CA	Warm	1.02	1.65	0.84	1.23	0.47	1.40	0.38	0.97	0.22	0.30	0.00	0.00	0.00	0.042
Three Sisters Wilderness, OR	Cold	0.41	0.37	0.27	0.26	0.14	0.21	0.12	0.15	0.06	0.05	0.00	0.00	0.00	0.008
Three Sisters Wilderness, OR	Warm	0.34	0.68	0.40	0.55	0.23	0.70	0.15	0.67	0.09	0.18	0.00	0.00	0.00	0.005
Tonto NM, AZ	Cold	0.29	0.39	0.27	0.37	0.14	0.57	0.12	0.40	0.10	0.15	0.05	0.07	0.00	0.015
Tonto NM, AZ	Warm	0.27	0.94	0.62	1.33	0.47	1.62	0.37	0.90	0.28	0.39	0.19	0.20	0.08	0.006
Upper Buffalo Wilderness, AK	Cold	0.33	0.50	0.30	0.48	0.22	0.84	0.17	0.70	0.11	0.21	0.06	0.06	0.00	0.014
Upper Buffalo Wilderness, AK	Warm	0.31	0.58	0.34	0.84	0.35	1.38	0.29	1.13	0.22	0.35	0.11	0.10	0.04	0.007
Washington, DC	Cold	1.03	1.31	0.80	0.77	0.48	0.97	0.35	0.91	0.29	0.27	0.00	0.00	0.00	0.070
Washington, DC	Warm	0.26	0.54	0.36	0.98	0.36	1.23	0.39	0.98	0.28	0.42	0.22	0.00	0.00	0.030
Weminuche Wilderness, CO	Cold	0.27	0.30	0.19	0.20	0.10	0.24	0.10	0.17	0.06	0.06	0.00	0.00	0.00	0.018
Weminuche Wilderness, CO	Warm	0.38	1.01	0.23	0.42	0.15	0.53	0.13	0.30	0.08	0.10	0.05	0.00	0.00	0.010
Yellowstone NP, CA	Cold	0.35	0.36	0.27	0.22	0.14	0.24	0.13	0.20	0.10	0.07	0.00	0.00	0.00	0.012
Yellowstone NP, CA	Warm	0.41	0.49	0.30	0.41	0.21	0.85	0.17	0.69	0.10	0.18	0.00	0.00	0.00	0.008
Yosemite NP, CA	Cold	0.33	0.39	0.23	0.32	0.16	0.56	0.16	0.32	0.09	0.14	0.00	0.00	0.00	0.006
Yosemite NP, CA	Warm	0.47	1.02	0.39	0.82	0.27	1.53	0.24	0.72	0.14	0.22	0.00	0.00	0.00	0.007
Yosemite NP, CA	10/25/95	26.16	48.04	17.97	84.75	16.34	88.99	9.74	43.50	4.52	11.42	0.98	0.00	0.00	0.626

Table A.4. Ambient Concentrations of Selected Fine Particle Chemical Species - Rochester to Yosemite (all values in ng/m³)

Site	Composite Sample	Acphenanthrylene	Pyrene	Retene	Benzo(ghi)fluoranthene	Cyclopenta(cd)pyrene	Benz(a)anthracene	Chrysene/Triphenylene	Benzo(k)fluoranthene	Benzo(b)fluoranthene	Benzo(i)fluoranthene	Benzo(e)pyrene	Benzo(a)pyrene	Perylene	Indeno(cd)pyrene
Rochester, NY	Cold	0.017	0.417	0.077	0.244	0.016	0.096	0.437	0.435	0.435	0.007	0.410	0.090	0.014	0.240
Rochester, NY	Warm	0.006	0.134	0.000	0.060	0.006	0.029	0.203	0.110	0.181	0.000	0.152	0.037	0.000	0.094
Rocky Mountain NP, CO	Cold	0.001	0.007	0.029	0.005	0.001	0.002	0.006	0.009	0.013	0.000	0.011	0.005	0.000	0.008
Rocky Mountain NP, CO	Warm	0.000	0.005	0.019	0.003	0.000	0.001	0.004	0.005	0.008	0.000	0.010	0.002	0.000	0.008
San Geronio Wilderness, CA	Cold	0.002	0.010	0.045	0.007	0.001	0.004	0.009	0.015	0.016	0.000	0.016	0.005	0.000	0.013
San Geronio Wilderness, CA	Warm	0.000	0.009	0.016	0.005	0.000	0.002	0.006	0.005	0.005	0.000	0.010	0.002	0.000	0.004
Sequoia NP, CA	Cold	0.031	0.084	4.079	0.053	0.022	0.156	0.340	0.113	0.134	0.034	0.114	0.122	0.026	0.089
Sequoia NP, CA	Warm	0.000	0.017	0.071	0.005	0.000	0.002	0.007	0.020	0.022	0.000	0.019	0.007	0.000	0.018
Sequoia NP, CA	11/11/95	0.050	0.153	0.933	0.116	0.000	0.138	0.409	0.237	0.327	0.000	0.494	0.253	0.000	0.181
Sequoia NP, CA	11/29/95	0.060	0.201	9.464	0.246	0.000	0.344	0.867	0.661	0.707	0.000	0.686	0.446	0.153	0.309
Shenandoah NP, VA	Cold	0.005	0.038	0.035	0.015	0.004	0.012	0.043	0.058	0.091	0.003	0.068	0.023	0.000	0.040
Shenandoah NP, VA	Warm	0.001	0.015	0.028	0.007	0.001	0.004	0.012	0.020	0.024	0.000	0.024	0.010	0.000	0.021
Shining Rock Wilderness, NC	Cold	0.003	0.016	0.015	0.007	0.002	0.005	0.013	0.018	0.023	0.000	0.022	0.009	0.000	0.017
Shining Rock Wilderness, NC	Warm	0.000	0.011	0.005	0.004	0.000	0.002	0.009	0.007	0.014	0.000	0.015	0.004	0.000	0.008
Sipsy Wilderness, AL	Cold	0.007	0.050	0.042	0.021	0.006	0.019	0.054	0.077	0.110	0.007	0.083	0.036	0.005	0.068
Sipsy Wilderness, AL	Warm	0.002	0.022	0.015	0.008	0.001	0.004	0.015	0.023	0.033	0.000	0.032	0.012	0.003	0.025
Snoqualmie National Forest, WA	Cold	0.002	0.015	0.047	0.009	0.002	0.005	0.018	0.027	0.033	0.000	0.024	0.010	0.000	0.016
Snoqualmie National Forest, WA	Warm	0.001	0.009	0.027	0.005	0.000	0.000	0.006	0.010	0.013	0.000	0.015	0.003	0.000	0.006
South Lake Tahoe, CA	Cold	0.049	0.323	2.263	0.418	0.158	0.501	0.805	1.000	0.753	0.127	0.744	0.713	0.110	0.753
South Lake Tahoe, CA	Warm	0.008	0.062	0.206	0.070	0.017	0.047	0.096	0.226	0.229	0.014	0.226	0.105	0.018	0.258
Three Sisters Wilderness, OR	Cold	0.001	0.008	0.060	0.004	0.000	0.002	0.006	0.006	0.010	0.000	0.010	0.004	0.000	0.006
Three Sisters Wilderness, OR	Warm	0.002	0.007	0.019	0.003	0.000	0.002	0.006	0.008	0.012	0.000	0.014	0.003	0.000	0.008
Tonto NM, AZ	Cold	0.002	0.013	0.253	0.007	0.000	0.004	0.015	0.020	0.018	0.004	0.018	0.007	0.000	0.015
Tonto NM, AZ	Warm	0.001	0.005	0.166	0.004	0.002	0.002	0.006	0.007	0.008	0.000	0.014	0.003	0.000	0.008
Upper Buffalo Wilderness, AK	Cold	0.004	0.016	0.033	0.009	0.002	0.006	0.019	0.029	0.032	0.003	0.032	0.013	0.000	0.029
Upper Buffalo Wilderness, AK	Warm	0.002	0.008	0.015	0.004	0.000	0.002	0.007	0.006	0.011	0.000	0.014	0.004	0.001	0.007
Washington, DC	Cold	0.015	0.077	0.046	0.067	0.018	0.065	0.162	0.280	0.266	0.023	0.269	0.156	0.023	0.225
Washington, DC	Warm	0.004	0.037	0.014	0.017	0.003	0.010	0.035	0.059	0.071	0.000	0.073	0.022	0.004	0.048
Weminuche Wilderness, CO	Cold	0.002	0.019	0.039	0.010	0.002	0.006	0.014	0.030	0.015	0.000	0.019	0.008	0.000	0.019
Weminuche Wilderness, CO	Warm	0.002	0.013	0.022	0.006	0.000	0.004	0.008	0.013	0.010	0.000	0.014	0.004	0.000	0.011
Yellowstone NP, CA	Cold	0.002	0.016	0.187	0.013	0.002	0.007	0.015	0.030	0.018	0.002	0.023	0.014	0.001	0.019
Yellowstone NP, CA	Warm	0.001	0.011	0.016	0.007	0.000	0.002	0.004	0.008	0.008	0.000	0.015	0.005	0.000	0.011
Yosemite NP, CA	Cold	0.000	0.012	0.042	0.007	0.000	0.000	0.005	0.005	0.006	0.003	0.009	0.002	0.000	0.004
Yosemite NP, CA	Warm	0.000	0.016	0.037	0.011	0.000	0.002	0.004	0.006	0.007	0.003	0.010	0.003	0.000	0.006
Yosemite NP, CA	10/25/95	0.082	0.663	26.205	0.366	0.147	0.884	1.849	0.753	0.842	0.116	1.085	0.604	0.144	0.416

Table A.4. Ambient Concentrations of Selected Fine Particle Chemical Species - Rochester to Yosemite (all values in ng/m³)

Site	Composite Sample	Benzo(ghi)perylene	Indeno(1,2,3-cd)fluoranthene	Dibenz[a,h]anthracene	Coronene	22,29,30-Trisnorhopane	22,29,30-Trisnorhopane	17a(H)-21b(H)-29-Norhopane	18a(H)-29-Norhopane	17b(H)-21a(H)-Normorethane	17a(H)-21b(H)-Hopane	17b(H),21a(H)-Morethane	22S, 17a(H),21b(H)-Homohopane	22R, 17a(H),21b(H)-Homohopane	22S, 17a(H),21b(H)-Bishomohopane
Rochester, NY	Cold	0.488	0.106	0.020	1.176	0.100	0.084	0.376	0.075	0.000	0.412	0.044	0.154	0.132	0.096
Rochester, NY	Warm	0.194	0.036	0.007	0.580	0.098	0.077	0.321	0.072	0.000	0.337	0.000	0.131	0.119	0.065
Rocky Mountain NP, CO	Cold	0.016	0.004	0.001	0.041	0.011	0.015	0.045	0.009	0.000	0.056	0.000	0.015	0.015	0.010
Rocky Mountain NP, CO	Warm	0.016	0.004	0.001	0.045	0.011	0.012	0.040	0.007	0.000	0.055	0.006	0.016	0.011	0.010
San Geronio Wilderness, CA	Cold	0.012	0.005	0.002	0.042	0.009	0.006	0.031	0.006	0.000	0.054	0.000	0.012	0.007	0.000
San Geronio Wilderness, CA	Warm	0.009	0.002	0.000	0.029	0.011	0.008	0.044	0.012	0.000	0.057	0.000	0.018	0.013	0.008
Sequoia NP, CA	Cold	0.077	0.033	0.026	0.074	0.014	0.021	0.127	0.011	0.000	0.072	0.000	0.052	0.029	0.040
Sequoia NP, CA	Warm	0.028	0.009	0.005	0.071	0.018	0.024	0.152	0.026	0.000	0.181	0.000	0.087	0.075	0.052
Sequoia NP, CA	11/11/95	0.214	0.125	0.000	0.000	0.000	0.000	0.534	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sequoia NP, CA	11/29/95	0.359	0.206	0.082	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Shenandoah NP, VA	Cold	0.053	0.018	0.006	0.101	0.011	0.010	0.052	0.014	0.000	0.060	0.000	0.023	0.019	0.013
Shenandoah NP, VA	Warm	0.029	0.010	0.002	0.053	0.015	0.008	0.040	0.008	0.000	0.049	0.000	0.019	0.021	0.013
Shining Rock Wilderness, NC	Cold	0.023	0.007	0.000	0.065	0.008	0.013	0.059	0.015	0.000	0.068	0.000	0.030	0.025	0.017
Shining Rock Wilderness, NC	Warm	0.011	0.000	0.000	0.026	0.015	0.010	0.041	0.015	0.000	0.050	0.000	0.022	0.023	0.015
Sipsy Wilderness, AL	Cold	0.086	0.024	0.009	0.196	0.008	0.011	0.060	0.023	0.000	0.085	0.000	0.040	0.033	0.028
Sipsy Wilderness, AL	Warm	0.038	0.009	0.003	0.087	0.014	0.010	0.042	0.000	0.000	0.058	0.000	0.036	0.031	0.020
Snoqualmie National Forest, WA	Cold	0.026	0.008	0.000	0.047	0.010	0.008	0.061	0.007	0.000	0.062	0.005	0.029	0.022	0.019
Snoqualmie National Forest, WA	Warm	0.013	0.000	0.000	0.025	0.011	0.011	0.055	0.013	0.000	0.069	0.000	0.029	0.021	0.011
South Lake Tahoe, CA	Cold	1.322	0.300	0.083	2.992	0.045	0.073	0.160	0.041	0.000	0.208	0.025	0.084	0.069	0.036
South Lake Tahoe, CA	Warm	0.586	0.110	0.020	1.835	0.057	0.066	0.235	0.064	0.000	0.304	0.041	0.120	0.090	0.063
Three Sisters Wilderness, OR	Cold	0.010	0.002	0.000	0.027	0.016	0.016	0.064	0.014	0.000	0.061	0.000	0.023	0.024	0.019
Three Sisters Wilderness, OR	Warm	0.014	0.004	0.001	0.033	0.011	0.012	0.057	0.016	0.000	0.070	0.000	0.025	0.017	0.010
Tonto NM, AZ	Cold	0.021	0.006	0.004	0.052	0.007	0.000	0.031	0.000	0.000	0.042	0.000	0.010	0.009	0.000
Tonto NM, AZ	Warm	0.013	0.003	0.003	0.037	0.011	0.008	0.039	0.000	0.000	0.052	0.000	0.016	0.011	0.008
Upper Buffalo Wilderness, AK	Cold	0.035	0.014	0.004	0.074	0.007	0.000	0.030	0.005	0.000	0.044	0.000	0.014	0.008	0.000
Upper Buffalo Wilderness, AK	Warm	0.013	0.003	0.001	0.031	0.010	0.006	0.031	0.007	0.000	0.043	0.000	0.014	0.011	0.000
Washington, DC	Cold	0.415	0.081	0.021	0.884	0.089	0.098	0.433	0.064	0.000	0.451	0.035	0.216	0.190	0.116
Washington, DC	Warm	0.124	0.018	0.006	0.315	0.023	0.022	0.144	0.034	0.000	0.215	0.017	0.117	0.098	0.079
Weminuche Wilderness, CO	Cold	0.026	0.008	0.000	0.056	0.011	0.010	0.041	0.008	0.000	0.045	0.006	0.018	0.016	0.007
Weminuche Wilderness, CO	Warm	0.022	0.006	0.000	0.059	0.011	0.010	0.042	0.008	0.000	0.049	0.005	0.017	0.010	0.006
Yellowstone NP, CA	Cold	0.028	0.008	0.000	0.046	0.014	0.018	0.087	0.018	0.000	0.099	0.009	0.050	0.039	0.032
Yellowstone NP, CA	Warm	0.041	0.006	0.000	0.132	0.013	0.014	0.055	0.015	0.000	0.068	0.008	0.028	0.023	0.018
Yosemite NP, CA	Cold	0.007	0.000	0.000	0.000	0.019	0.016	0.130	0.026	0.000	0.135	0.013	0.106	0.082	0.069
Yosemite NP, CA	Warm	0.011	0.003	0.000	0.033	0.021	0.018	0.144	0.023	0.000	0.155	0.000	0.112	0.093	0.082
Yosemite NP, CA	10/25/95	0.557	0.484	0.095	0.928	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table A.4. Ambient Concentrations of Selected Fine Particle Chemical Species - Rochester to Yosemite (all values in ng/m³)

Site	Composite Sample	22R, 17a(H),21b(H)- Bishomohopane	22S, 17a(H),21b(H)- Trishomohopane	22R, 17a(H),21b(H)- Trishomohopane	20R+S, abb-Cholestane	20R, aaa-Cholestane	20R+S, abb-Ergostane	20R+S, abb-Sitostane	1H-Phenalen-1-one	Anthracen-9,10-dione	Benz(de)anthracen-7-one	Benz(a)anthracen-7,12- dione	Dibenzofuran	Squalene	Nonanal
Rochester, NY	Cold	0.075	0.054	0.036	0.207	0.159	0.115	0.213	0.187	0.777	0.298	0.161	0.00	0.42	1.92
Rochester, NY	Warm	0.051	0.042	0.029	0.167	0.137	0.101	0.158	0.031	0.879	0.055	0.090	0.00	0.30	10.07
Rocky Mountain NP, CO	Cold	0.011	0.000	0.000	0.028	0.022	0.000	0.026	0.000	0.000	0.012	0.000	0.00	0.74	0.00
Rocky Mountain NP, CO	Warm	0.008	0.000	0.000	0.028	0.023	0.000	0.033	0.000	0.000	0.008	0.000	0.00	0.72	0.00
San Geronio Wilderness, CA	Cold	0.000	0.000	0.000	0.000	0.011	0.000	0.017	0.013	0.014	0.025	0.011	0.00	0.44	0.00
San Geronio Wilderness, CA	Warm	0.008	0.000	0.000	0.029	0.019	0.000	0.025	0.000	0.010	0.004	0.000	0.00	0.65	0.00
Sequoia NP, CA	Cold	0.026	0.000	0.000	0.000	0.000	0.000	0.051	0.161	0.142	0.000	0.000	0.00	0.76	0.00
Sequoia NP, CA	Warm	0.041	0.052	0.028	0.061	0.038	0.079	0.092	0.000	0.000	0.000	0.000	0.00	0.69	0.00
Sequoia NP, CA	11/11/95	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00	18.98	0.00
Sequoia NP, CA	11/29/95	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.33	12.34	0.00
Shenandoah NP, VA	Cold	0.011	0.000	0.000	0.020	0.017	0.000	0.023	0.000	0.017	0.039	0.022	0.00	0.82	0.00
Shenandoah NP, VA	Warm	0.010	0.000	0.000	0.025	0.000	0.000	0.024	0.000	0.000	0.000	0.000	0.00	0.34	0.00
Shining Rock Wilderness, NC	Cold	0.014	0.012	0.000	0.025	0.020	0.000	0.025	0.000	0.000	0.000	0.000	0.00	0.59	0.00
Shining Rock Wilderness, NC	Warm	0.019	0.008	0.000	0.000	0.000	0.000	0.021	0.000	0.000	0.000	0.000	0.00	0.24	0.00
Sipsy Wilderness, AL	Cold	0.023	0.018	0.011	0.018	0.000	0.000	0.029	0.014	0.019	0.055	0.042	0.01	0.73	0.00
Sipsy Wilderness, AL	Warm	0.000	0.022	0.008	0.000	0.000	0.000	0.021	0.000	0.014	0.000	0.000	0.01	0.60	0.00
Snoqualmie National Forest, WA	Cold	0.014	0.012	0.007	0.020	0.014	0.000	0.022	0.000	0.008	0.011	0.000	0.00	0.64	0.00
Snoqualmie National Forest, WA	Warm	0.013	0.007	0.006	0.026	0.019	0.000	0.022	0.000	0.000	0.000	0.000	0.00	1.51	0.00
South Lake Tahoe, CA	Cold	0.035	0.030	0.000	0.153	0.104	0.000	0.136	0.408	0.151	1.382	0.261	0.01	1.72	0.59
South Lake Tahoe, CA	Warm	0.051	0.037	0.021	0.187	0.146	0.116	0.173	0.035	0.027	0.268	0.074	0.00	1.19	0.53
Three Sisters Wilderness, OR	Cold	0.011	0.010	0.000	0.041	0.024	0.000	0.031	0.000	0.000	0.000	0.000	0.00	0.61	0.13
Three Sisters Wilderness, OR	Warm	0.010	0.006	0.000	0.036	0.026	0.026	0.034	0.000	0.000	0.000	0.000	0.00	0.77	0.00
Tonto NM, AZ	Cold	0.000	0.000	0.000	0.000	0.000	0.000	0.016	0.000	0.000	0.010	0.000	0.00	0.61	0.34
Tonto NM, AZ	Warm	0.000	0.000	0.000	0.000	0.000	0.000	0.022	0.000	0.000	0.000	0.000	0.00	0.56	0.00
Upper Buffalo Wilderness, AK	Cold	0.000	0.000	0.000	0.000	0.000	0.000	0.021	0.017	0.017	0.048	0.022	0.00	0.54	0.00
Upper Buffalo Wilderness, AK	Warm	0.000	0.000	0.000	0.000	0.000	0.000	0.016	0.000	0.000	0.000	0.000	0.00	0.38	0.00
Washington, DC	Cold	0.103	0.089	0.061	0.185	0.139	0.145	0.248	0.085	0.063	0.307	0.151	0.01	0.80	0.00
Washington, DC	Warm	0.059	0.056	0.037	0.058	0.045	0.054	0.102	0.000	0.017	0.029	0.033	0.00	0.44	0.00
Weminuche Wilderness, CO	Cold	0.007	0.000	0.000	0.022	0.014	0.000	0.027	0.000	0.000	0.011	0.000	0.00	0.68	0.00
Weminuche Wilderness, CO	Warm	0.007	0.000	0.000	0.030	0.026	0.000	0.023	0.005	0.000	0.000	0.000	0.00	0.61	0.00
Yellowstone NP, CA	Cold	0.021	0.019	0.013	0.027	0.025	0.000	0.038	0.007	0.000	0.000	0.000	0.00	0.65	0.00
Yellowstone NP, CA	Warm	0.015	0.012	0.007	0.037	0.024	0.000	0.030	0.004	0.000	0.000	0.000	0.00	0.52	0.00
Yosemite NP, CA	Cold	0.051	0.058	0.038	0.020	0.022	0.000	0.041	0.004	0.000	0.000	0.000	0.00	1.05	0.00
Yosemite NP, CA	Warm	0.059	0.069	0.043	0.031	0.028	0.000	0.057	0.000	0.000	0.000	0.000	0.00	0.70	0.00
Yosemite NP, CA	10/25/95	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.671	0.000	0.33	8.78	0.00

Table A.4. Ambient Concentrations of Selected Fine Particle Chemical Species - Rochester to Yosemite (all values in ng/m³)

Site	Composite Sample	Levoglucosan	8,15-Pimaradienoic Acid	Pimaric Acid	Sandaracopimaric Acid	Isopimaric Acid	Dehydroabietic Acid	Abietic Acid	Abieta-8,11,13,15-pentatrien-18-oic Acid	Abieta-8,11,13-tetraen-18-oic Acid	Abieta-8,11,13,15-tetraen-18-oic Acid	7-Oxodehydroabietic Acid	Octanoic Acid	Nonanoic Acid	Decanoic Acid
Rochester, NY	Cold	71.1	0.01	0.04	0.01	0.02	0.57	0.00	0.00	0.10	0.04	0.13	0.67	1.68	1.20
Rochester, NY	Warm	30.3	0.00	0.00	0.00	0.00	0.25	0.00	0.13	0.08	0.05	0.10	0.46	1.45	1.42
Rocky Mountain NP, CO	Cold	6.3	0.05	0.11	0.03	0.14	1.96	0.02	0.02	0.31	0.11	0.22	0.36	0.67	1.05
Rocky Mountain NP, CO	Warm	22.6	0.09	0.19	0.04	0.23	5.21	0.00	0.02	0.59	0.20	0.47	0.39	0.55	0.77
San Geronio Wilderness, CA	Cold	0.0	0.15	0.08	0.03	0.28	1.29	0.01	0.04	0.38	0.18	0.16	0.21	0.61	0.74
San Geronio Wilderness, CA	Warm	5.0	0.06	0.02	0.01	0.02	2.13	0.00	0.00	0.13	0.05	0.13	0.11	0.18	0.35
Sequoia NP, CA	Cold	404.6	3.63	3.25	2.02	6.73	60.97	2.16	2.67	32.85	8.91	10.18	0.17	0.66	0.59
Sequoia NP, CA	Warm	54.7	0.22	0.21	0.20	0.50	11.22	0.00	0.09	2.39	0.67	1.74	0.17	0.30	0.51
Sequoia NP, CA	11/11/95	1901.8	1.70	2.23	1.65	4.34	56.91	1.07	0.63	15.85	3.37	7.15	10.32	11.71	4.49
Sequoia NP, CA	11/29/95	2719.5	18.55	18.99	14.00	29.74	432.39	0.00	7.86	107.66	24.93	28.50	0.00	33.65	0.00
Shenandoah NP, VA	Cold	42.6	0.05	0.06	0.02	0.06	1.19	0.00	0.04	0.18	0.09	0.20	0.21	0.39	0.71
Shenandoah NP, VA	Warm	0.0	0.00	0.05	0.01	0.06	0.77	0.00	0.10	0.38	0.08	0.24	0.10	0.51	0.49
Shining Rock Wilderness, NC	Cold	19.6	0.00	0.00	0.04	0.00	0.53	0.00	0.00	0.12	0.11	0.11	0.00	0.40	0.30
Shining Rock Wilderness, NC	Warm	0.0	0.06	0.01	0.00	0.00	0.17	0.00	0.03	0.12	0.02	0.12	0.14	0.47	0.47
Sipsy Wilderness, AL	Cold	75.7	0.00	0.07	0.04	0.00	2.28	0.00	0.12	0.58	0.36	0.56	0.00	0.26	0.25
Sipsy Wilderness, AL	Warm	34.4	0.00	0.02	0.00	0.09	0.76	0.00	0.13	0.71	0.19	0.60	0.19	0.39	0.55
Snoqualmie National Forest, WA	Cold	24.3	0.03	0.04	0.02	0.07	0.92	0.00	0.02	0.17	0.08	0.29	0.45	0.80	1.17
Snoqualmie National Forest, WA	Warm	21.5	0.00	0.00	0.01	0.02	0.41	0.00	0.00	0.07	0.02	0.09	0.45	0.49	0.99
South Lake Tahoe, CA	Cold	488.8	7.15	5.71	1.91	13.73	87.57	4.87	0.82	17.69	5.96	6.56	0.00	0.77	0.59
South Lake Tahoe, CA	Warm	125.1	0.52	0.64	0.24	1.75	15.05	0.15	0.14	2.43	0.71	1.72	0.37	0.91	0.94
Three Sisters Wilderness, OR	Cold	15.4	0.03	0.04	0.02	0.08	0.91	0.00	0.00	0.18	0.10	0.28	0.47	0.73	0.98
Three Sisters Wilderness, OR	Warm	34.6	0.01	0.01	0.03	0.05	1.04	0.00	0.02	0.15	0.08	0.31	0.37	0.33	0.60
Tonto NM, AZ	Cold	17.2	0.28	0.31	0.09	0.35	5.30	0.02	0.05	1.18	0.44	0.82	0.22	0.50	0.71
Tonto NM, AZ	Warm	14.8	0.16	0.27	0.06	0.25	5.84	0.00	0.07	1.20	0.74	0.84	0.15	0.33	0.53
Upper Buffalo Wilderness, AK	Cold	50.5	0.01	0.04	0.02	0.02	0.72	0.00	0.03	0.14	0.07	0.32	0.18	0.51	0.75
Upper Buffalo Wilderness, AK	Warm	30.4	0.00	0.00	0.00	0.00	0.56	0.00	0.05	0.18	0.12	0.27	0.00	0.00	0.41
Washington, DC	Cold	105.6	0.05	0.08	0.02	0.11	1.63	0.00	0.06	0.30	0.13	0.34	0.16	0.33	0.44
Washington, DC	Warm	27.7	0.00	0.00	0.00	0.00	0.45	0.00	0.06	0.19	0.10	0.29	0.00	0.00	0.39
Weminuche Wilderness, CO	Cold	5.1	0.13	0.03	0.01	0.04	0.60	0.00	0.00	0.10	0.03	0.08	0.38	1.05	1.43
Weminuche Wilderness, CO	Warm	5.4	0.02	0.01	0.01	0.04	0.42	0.00	0.01	0.08	0.03	0.09	0.27	0.44	0.76
Yellowstone NP, CA	Cold	30.2	0.36	0.50	0.11	0.77	9.42	0.15	0.04	1.53	0.42	0.53	0.17	0.59	0.81
Yellowstone NP, CA	Warm	16.3	0.02	0.06	0.02	0.07	1.09	0.00	0.01	0.18	0.06	0.18	0.23	0.57	0.69
Yosemite NP, CA	Cold	23.3	0.07	0.03	0.13	0.11	1.86	0.00	0.02	0.44	0.07	0.30	0.23	0.35	0.57
Yosemite NP, CA	Warm	24.2	0.11	0.06	0.21	0.22	3.54	0.00	0.04	0.88	0.25	0.63	0.00	0.22	0.35
Yosemite NP, CA	10/25/95	2906.5	16.85	11.02	6.85	36.59	165.85	14.90	4.78	78.83	20.99	17.35	7.44	10.64	6.95

Table A.4. Ambient Concentrations of Selected Fine Particle Chemical Species - Rochester to Yosemite (all values in ng/m³)

Site	Composite Sample	Undecanoic Acid	Dodecanoic Acid	Tridecanoic Acid	Tetradecanoic Acid	Pentadecanoic Acid	Hexadecanoic Acid	Heptadecanoic Acid	Octadecanoic Acid	Nonadecanoic Acid	Eicosanoic Acid	Heneicosanoic Acid	Docosanoic Acid	Tricosanoic Acid	Tetracosanoic Acid
Rochester, NY	Cold	0.39	2.56	0.53	1.96	1.06	16.10	0.67	7.36	0.27	1.00	0.52	2.56	0.78	2.88
Rochester, NY	Warm	0.36	6.65	1.02	3.35	1.20	13.62	0.63	6.00	0.31	2.00	0.44	2.78	0.73	2.60
Rocky Mountain NP, CO	Cold	0.17	1.84	0.29	2.33	1.02	6.76	0.37	4.24	0.07	0.42	0.09	0.73	0.18	0.83
Rocky Mountain NP, CO	Warm	0.15	1.51	0.24	2.21	1.13	8.17	0.42	3.73	0.11	0.83	0.18	1.57	0.33	1.56
San Geronio Wilderness, CA	Cold	0.13	1.76	0.31	2.01	0.81	5.53	0.32	3.57	0.07	0.32	0.09	0.73	0.16	0.77
San Geronio Wilderness, CA	Warm	0.09	1.24	0.28	2.28	1.06	8.43	0.49	3.81	0.16	0.46	0.14	0.78	0.24	1.01
Sequoia NP, CA	Cold	0.20	2.01	0.80	5.25	3.69	32.97	2.97	17.23	4.08	24.43	9.42	85.11	17.98	66.71
Sequoia NP, CA	Warm	0.11	1.28	0.35	1.91	0.87	8.76	0.69	8.01	0.67	5.74	1.30	20.95	2.55	11.41
Sequoia NP, CA	11/11/95	1.33	12.25	2.55	15.95	10.72	109.27	9.98	58.43	9.29	76.73	27.82	309.14	57.78	246.34
Sequoia NP, CA	11/29/95	0.00	0.00	0.00	21.80	0.00	132.51	8.59	78.91	12.55	112.89	0.00	440.73	35.33	277.13
Shenandoah NP, VA	Cold	0.13	1.58	0.25	1.69	0.80	5.98	0.36	3.56	0.14	0.61	0.33	1.73	0.62	2.62
Shenandoah NP, VA	Warm	0.00	1.14	0.19	1.49	0.82	8.62	0.47	4.18	0.22	2.14	0.52	3.43	0.91	3.63
Shining Rock Wilderness, NC	Cold	0.00	1.21	0.14	1.75	0.53	6.87	0.30	5.26	0.00	0.31	0.00	0.67	0.18	0.98
Shining Rock Wilderness, NC	Warm	0.07	1.26	0.20	1.58	0.95	8.23	0.44	4.71	0.15	1.15	0.26	1.72	0.54	1.85
Sipsy Wilderness, AL	Cold	0.00	1.16	0.18	1.64	0.73	8.68	0.41	5.59	0.00	0.61	0.00	1.40	0.58	2.52
Sipsy Wilderness, AL	Warm	0.00	1.03	0.18	1.22	0.66	6.11	0.35	4.42	0.16	0.98	0.26	1.68	0.65	2.61
Snoqualmie National Forest, WA	Cold	0.16	1.75	0.28	1.87	0.80	4.58	0.28	3.23	0.10	0.68	0.14	1.74	0.23	1.73
Snoqualmie National Forest, WA	Warm	0.16	1.83	0.28	2.37	1.07	6.11	0.30	3.14	0.15	1.09	0.23	1.67	0.35	1.48
South Lake Tahoe, CA	Cold	0.00	3.31	0.77	3.33	1.43	21.33	1.30	10.38	0.93	7.61	0.00	22.66	1.94	16.45
South Lake Tahoe, CA	Warm	0.28	3.26	0.65	3.21	1.55	15.83	0.96	10.28	0.51	2.88	0.72	8.09	1.23	6.54
Three Sisters Wilderness, OR	Cold	0.14	1.86	0.30	2.32	0.98	5.61	0.28	3.43	0.08	0.61	0.14	1.59	0.25	1.75
Three Sisters Wilderness, OR	Warm	0.12	1.23	0.25	2.42	1.12	8.66	0.43	3.81	0.21	1.56	0.42	3.82	0.77	4.38
Tonto NM, AZ	Cold	0.15	1.73	0.29	1.69	0.81	5.24	0.35	3.40	0.11	0.90	0.20	2.01	0.44	2.04
Tonto NM, AZ	Warm	0.11	1.29	0.24	1.89	1.11	8.74	0.59	5.44	0.29	1.37	0.30	2.82	0.67	2.88
Upper Buffalo Wilderness, AK	Cold	0.15	1.53	0.27	1.82	1.05	6.59	0.35	3.84	0.17	0.77	0.47	2.31	0.99	4.39
Upper Buffalo Wilderness, AK	Warm	0.08	1.08	0.10	1.49	0.79	6.21	0.35	4.18	0.15	1.45	0.00	2.19	0.72	2.75
Washington, DC	Cold	0.11	1.35	0.28	1.95	0.93	10.63	0.59	6.98	0.27	1.08	0.66	3.31	1.18	5.41
Washington, DC	Warm	0.00	0.87	0.10	1.46	0.62	7.61	0.35	5.94	0.21	1.57	0.00	2.45	0.71	2.43
Weminuche Wilderness, CO	Cold	0.21	1.89	0.26	1.56	0.66	4.17	0.26	2.67	0.06	0.30	0.09	0.63	0.15	0.73
Weminuche Wilderness, CO	Warm	0.15	1.64	0.28	1.98	0.74	5.17	0.26	2.46	0.11	0.51	0.19	1.24	0.29	1.31
Yellowstone NP, CA	Cold	0.13	2.13	0.26	1.95	0.80	6.51	0.35	3.67	0.09	0.88	0.14	1.40	0.21	0.99
Yellowstone NP, CA	Warm	0.13	1.72	0.26	2.26	1.06	7.77	0.39	4.05	0.13	0.86	0.21	1.49	0.37	1.23
Yosemite NP, CA	Cold	0.13	1.81	0.30	1.95	0.80	5.81	0.40	3.53	0.21	1.52	0.40	6.73	0.80	3.71
Yosemite NP, CA	Warm	0.07	1.17	0.29	2.13	0.97	15.22	0.85	7.63	0.45	2.73	0.00	12.63	1.19	5.81
Yosemite NP, CA	10/25/95	2.30	25.96	7.36	47.41	32.28	237.56	22.72	88.50	21.49	120.64	47.43	472.63	84.67	355.76

Table A.4. Ambient Concentrations of Selected Fine Particle Chemical Species - Rochester to Yosemite (all values in ng/m³)

Site	Composite Sample	Pentacosanoic Acid	Hexacosanoic Acid	Heptacosanoic Acid	Octacosanoic Acid	Nonacosanoic Acid	Triacontanoic Acid	Hentriacontanoic Acid	Dotriacontanoic Acid	9-Hexadecenoic Acid	9,12-Octadecanedienoic Acid	9-Octadecenoic Acid	Propanedioic Acid	Methylpropanedioic Acid	Butanedioic Acid
Rochester, NY	Cold	0.40	1.26	0.15	0.61	0.10	0.36	0.04	0.13	0.34	0.33	1.23	3.63	0.00	11.47
Rochester, NY	Warm	0.44	1.55	0.26	1.44	0.18	0.95	0.06	0.27	0.28	0.17	0.47	9.40	0.87	21.11
Rocky Mountain NP, CO	Cold	0.10	0.38	0.04	0.19	0.03	0.14	0.00	0.05	2.01	0.24	1.26	0.00	0.00	2.00
Rocky Mountain NP, CO	Warm	0.18	0.69	0.10	0.57	0.06	0.46	0.01	0.11	1.82	0.65	1.67	0.61	0.00	5.19
San Geronio Wilderness, CA	Cold	0.10	0.31	0.04	0.20	0.03	0.11	0.00	0.03	1.76	0.33	1.25	1.86	0.21	11.09
San Geronio Wilderness, CA	Warm	0.18	0.57	0.12	0.56	0.08	0.41	0.03	0.10	1.90	0.29	1.42	3.16	0.34	15.88
Sequoia NP, CA	Cold	6.27	23.79	2.48	13.52	2.11	8.95	0.69	2.69	0.59	1.25	1.94	2.70	0.60	28.04
Sequoia NP, CA	Warm	0.84	2.27	0.37	1.68	0.28	1.90	0.13	0.69	1.18	0.59	1.19	7.62	0.58	25.44
Sequoia NP, CA	11/11/95	20.93	101.02	7.71	50.67	6.75	30.81	2.08	7.36	8.99	5.34	19.68	0.00	0.00	18.93
Sequoia NP, CA	11/29/95	9.05	22.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	18.95
Shenandoah NP, VA	Cold	0.31	1.35	0.13	0.66	0.11	0.51	0.04	0.18	1.32	0.31	1.18	1.26	0.00	8.39
Shenandoah NP, VA	Warm	0.48	1.83	0.27	1.29	0.18	0.88	0.07	0.27	0.66	0.33	0.65	15.02	0.64	18.19
Shining Rock Wilderness, NC	Cold	0.00	0.36	0.00	0.00	0.00	0.00	0.00	0.00	1.35	0.22	0.46	0.00	0.00	3.79
Shining Rock Wilderness, NC	Warm	0.33	1.09	0.20	0.92	0.13	0.70	0.05	0.25	0.28	0.29	0.44	7.97	0.00	6.83
Sipsy Wilderness, AL	Cold	0.00	0.93	0.00	0.00	0.00	0.00	0.00	0.00	1.19	0.49	0.93	1.31	0.00	7.27
Sipsy Wilderness, AL	Warm	0.42	1.63	0.26	1.29	0.21	1.12	0.09	0.41	1.00	1.32	1.34	8.28	0.38	19.37
Snoqualmie National Forest, WA	Cold	0.10	0.42	0.03	0.16	0.02	0.11	0.01	0.03	1.44	0.25	1.11	0.22	0.00	2.45
Snoqualmie National Forest, WA	Warm	0.17	0.48	0.07	0.27	0.04	0.18	0.01	0.06	2.01	0.53	1.73	0.34	0.00	3.31
South Lake Tahoe, CA	Cold	0.45	1.84	0.00	0.00	0.00	0.00	0.00	0.00	2.08	1.08	5.30	0.89	0.00	16.41
South Lake Tahoe, CA	Warm	0.46	1.40	0.20	0.73	0.13	0.58	0.05	0.16	2.34	0.46	2.48	2.59	0.35	15.03
Three Sisters Wilderness, OR	Cold	0.10	0.44	0.02	0.12	0.02	0.10	0.00	0.03	2.07	0.85	1.48	0.00	0.00	1.70
Three Sisters Wilderness, OR	Warm	0.35	1.56	0.15	0.69	0.10	0.54	0.04	0.18	2.36	1.44	1.89	0.99	0.11	4.78
Tonto NM, AZ	Cold	0.20	0.72	0.09	0.47	0.06	0.32	0.02	0.09	1.46	0.23	1.18	1.04	0.00	5.50
Tonto NM, AZ	Warm	0.35	1.14	0.19	1.11	0.15	0.99	0.05	0.22	1.38	0.28	1.39	1.37	0.00	6.31
Upper Buffalo Wilderness, AK	Cold	0.52	2.46	0.20	1.15	0.19	1.00	0.09	0.40	1.71	0.37	1.38	2.00	0.23	12.78
Upper Buffalo Wilderness, AK	Warm	0.38	1.48	0.20	1.09	0.13	0.85	0.00	0.26	1.44	1.07	1.81	14.48	1.24	19.08
Washington, DC	Cold	0.54	2.81	0.18	0.86	0.11	0.51	0.05	0.17	1.97	0.55	2.23	1.48	0.17	10.44
Washington, DC	Warm	0.39	1.30	0.21	0.87	0.00	0.46	0.00	0.00	1.14	0.35	1.23	10.48	1.23	20.11
Weminuche Wilderness, CO	Cold	0.10	0.29	0.04	0.16	0.02	0.09	0.00	0.02	1.89	0.19	1.27	0.22	0.00	1.42
Weminuche Wilderness, CO	Warm	0.16	0.53	0.08	0.43	0.05	0.26	0.02	0.05	1.81	0.47	1.41	0.58	0.00	3.28
Yellowstone NP, CA	Cold	0.08	0.25	0.03	0.12	0.01	0.09	0.00	0.03	1.74	0.40	1.67	0.16	0.00	1.12
Yellowstone NP, CA	Warm	0.19	0.61	0.10	0.52	0.07	0.33	0.02	0.08	1.95	0.85	1.80	0.78	0.00	5.07
Yosemite NP, CA	Cold	0.27	0.75	0.09	0.39	0.07	0.35	0.03	0.12	1.62	0.30	1.21	0.80	0.00	7.07
Yosemite NP, CA	Warm	0.40	0.95	0.16	0.49	0.00	0.45	0.00	0.00	1.15	0.41	1.19	4.01	0.00	12.57
Yosemite NP, CA	10/25/95	31.85	133.52	19.01	105.21	14.46	58.63	4.55	16.31	13.56	9.35	33.82	0.00	0.00	13.90

Table A.4. Ambient Concentrations of Selected Fine Particle Chemical Species - Rochester to Yosemite (all values in ng/m³)

Site	Composite Sample	Methylbutanedioic Acid	Pentanedioic Acid	Hexanedioic Acid	Heptanedioic Acid	Octanedioic Acid	Nonanedioic Acid
Rochester, NY	Cold	2.92	10.31	9.49	3.58	1.44	6.23
Rochester, NY	Warm	3.08	9.33	8.58	2.22	2.17	8.06
Rocky Mountain NP, CO	Cold	0.35	0.60	1.40	0.16	0.49	1.64
Rocky Mountain NP, CO	Warm	0.70	1.51	1.53	0.58	1.33	2.46
San Geronio Wilderness, CA	Cold	1.64	3.57	2.17	0.48	0.60	1.52
San Geronio Wilderness, CA	Warm	2.04	5.36	3.71	1.08	1.37	2.99
Sequoia NP, CA	Cold	5.96	6.43	4.70	1.93	1.85	9.48
Sequoia NP, CA	Warm	2.95	7.26	4.86	1.71	2.12	5.91
Sequoia NP, CA	11/11/95	6.92	6.84	4.38	3.82	9.17	46.83
Sequoia NP, CA	11/29/95	0.00	0.00	0.00	0.00	0.00	0.00
Shenandoah NP, VA	Cold	1.36	2.71	2.36	0.63	0.90	2.19
Shenandoah NP, VA	Warm	0.96	2.65	4.18	0.73	0.54	1.80
Shining Rock Wilderness, NC	Cold	0.00	0.00	0.00	0.00	0.00	0.00
Shining Rock Wilderness, NC	Warm	0.40	1.34	7.17	0.34	0.32	1.02
Sipsy Wilderness, AL	Cold	1.22	0.84	1.48	0.00	0.00	1.28
Sipsy Wilderness, AL	Warm	1.31	3.87	5.86	1.06	1.58	5.39
Snoqualmie National Forest, WA	Cold	0.61	0.87	0.92	0.18	0.63	1.32
Snoqualmie National Forest, WA	Warm	0.46	1.03	1.23	0.37	0.83	1.54
South Lake Tahoe, CA	Cold	5.60	2.74	1.64	0.00	0.98	13.96
South Lake Tahoe, CA	Warm	2.25	5.25	3.32	1.67	3.11	9.88
Three Sisters Wilderness, OR	Cold	0.33	0.49	1.07	0.20	0.69	1.48
Three Sisters Wilderness, OR	Warm	0.64	1.36	1.28	0.42	1.16	1.86
Tonto NM, AZ	Cold	0.88	1.60	1.65	0.43	1.15	2.19
Tonto NM, AZ	Warm	0.96	1.59	1.33	0.48	0.90	2.02
Upper Buffalo Wilderness, AK	Cold	1.75	3.42	2.13	0.82	1.44	2.88
Upper Buffalo Wilderness, AK	Warm	1.67	3.99	3.68	0.80	1.24	2.66
Washington, DC	Cold	1.83	3.34	2.15	1.22	1.25	4.76
Washington, DC	Warm	2.01	4.29	2.66	0.78	1.45	4.16
Weminuche Wilderness, CO	Cold	0.25	0.49	1.23	0.12	0.24	0.57
Weminuche Wilderness, CO	Warm	0.32	0.96	1.02	0.31	0.52	0.91
Yellowstone NP, CA	Cold	0.35	0.47	0.83	0.12	0.50	1.48
Yellowstone NP, CA	Warm	0.57	1.68	1.87	0.53	1.15	1.98
Yosemite NP, CA	Cold	0.87	2.02	1.89	0.47	0.90	1.64
Yosemite NP, CA	Warm	1.56	3.46	2.46	1.09	1.96	4.29
Yosemite NP, CA	10/25/95	4.58	6.11	5.20	4.34	14.73	56.08

Appendix B

Results from the VOC Analysis of the Wood Stove Source Tests

The following table provides results from the non-methane volatile hydrocarbon analysis of the wood stove emissions conducted by Rei Rasmussen at Biospheric Research Corporation. Samples were collected in polished stainless steel SUMA canisters which were filled continuously during the entire wood burning source test. The flow into the canisters was set at a constant flow rate and was filtered with a Teflon filter. Another SUMA canister sampled the dilution air and was used to blank correct the values given in Table B.1. Unfortunately, the VOC analysis from the fireplace source tests could not be performed due to difficulties with the analytical equipment and subsequent loss of the samples.

Table B.1. VOC Emissions from the Combustion of Fuelwood in a Wood Stove With and Without the Catalytic Bed Engaged (all values in mg compound per kg of wood burned)

Compound	White Oak Non-catalyst	White Oak Catalyst	Red Maple Non-catalyst	Sugar Maple Non-catalyst	Douglas Fir Non-catalyst	Douglas Fir Catalyst	Loblolly Pine Non-catalyst
Ethane	241	153	69.4	63.1	74.8	115	177
Ethylene	456	368	175	194	216	303	395
Acetylene	311	255	125	179	249	212	313
Propane	66.2	32.5	16.0	14.2	16.6	25.1	48.7
Propene	152	76.6	36.6	48.9	43.1	54.3	99.1
i-Butane	3.4	4.5	1.4	1.0	1.0	2.4	1.2
i-Butene	33.0	7.5	3.6	4.8	4.2	7.6	8.4
1-Butene	38.4	12.1	5.1	8.7	6.8	13.3	14.7
1,3-Butadiene	29.4	8.4	5.5	7.0	8.7	13.1	16.0
n-Butane	13.0	10.9	2.0	5.2	3.7	3.5	8.1
trans-2-Butene	16.9	13.1	5.8	5.8	-	5.8	-
cis-2-Butene	9.0	3.0	1.8	1.5	1.1	2.3	4.0
3-Methyl-1-butene	2.3	0.0	-	-	0.7	-	-
i-Pentane	3.0	7.8	2.3	3.6	1.4	1.8	1.9
2-Methyl-1-butene	3.9	0.0	-	-	1.1	-	-
n-Pentane	3.7	4.4	1.4	2.1	0.7	1.5	2.2
trans-2-Pentene	-	2.7	-	1.1	0.7	1.7	-
cis-2-Pentene	4.5	2.4	-	-	0.6	-	-
2-Methyl-2-butene	4.1	2.1	-	-	-	-	-
Cyclopentene	3.5	-	-	-	-	-	-
2-Methylpentane	-	-	-	-	0.6	-	-
1-Hexene	49.9	22.1	-	-	-	13.9	22.8
n-Hexane	3.4	2.8	1.2	2.0	0.8	-	-
Benzene	184	144	68.1	75.2	110	164	173
Toluene	72.6	45.8	18.0	23.1	27.9	50.4	49.8
Ethylbenzene	11.0	6.6	1.6	3.5	4.1	6.7	8.1
m-Xylene + p-Xylene	19.2	13.2	3.2	6.3	8.9	16.8	15.4
o-Xylene	7.2	4.7	1.5	2.8	2.6	4.1	7.1

Appendix C

Results from the Carbonyl Analysis of the Fireplace and Wood Stove Source Tests

The following tables show the results from the volatile and semi-volatile carbonyl analysis conducted by Eric Grosjean at DGA, Inc. Samples were collected downstream of the cyclone by two dinitrophenylhydrazine (DNPH) impregnated cartridges operated in series. The analysis results from both in-series cartridges from each test were summed to get the total carbonyl emissions. The flow through the cartridges was monitored throughout the test and were kept approximately constant. All blank samples were clean with respect to the compounds quantified.

Table C.1 includes the results from the top five nationally available wood species that were burned in the fireplace source tests. Table C.2 displays results from the same five wood species burned in the wood stove, including two tests with the wood stove's catalytic bed engaged.

Table C.1. Results of the Carbonyl Analysis for the Fireplace Combustion of Selected Woods (all values in milligram compound per kilogram wood burned)

Compound	Red Maple	Sugar Maple	Douglas Fir	Loblolly Pine	White Oak
<u>Aldehydes</u>					
formaldehyde	581	528	581	366	508
acetaldehyde	266	478	352	273	750
propanal	32.2	63.6	27.8	39.5	98.6
butanal and / or isobutanal	11.7	14.1	21.0	11.2	33.5
isopentanal	32.8	46.3	46.2	52.4	36.8
pentanal	32.8	20.7	21.0	33.9	19.5
hexanal	21.5	10.4	12.9	14.7	6.5
heptanal	1.5	2.6	1.7	2.7	2.5
octanal	5.8	3.5	2.0	1.8	3.1
nonanal	9.8	6.5	7.9	24.7	8.6
decanal	4.0	11.9	5.9	74.8	32.2
<u>Ketones</u>					
acetone	128	163	82.2	99.3	145
2-butanone	36.2	37.6	21.7	36.2	60.5
<u>Unsaturated Carbonyls</u>					
acrolein	17.2	6.0	9.7	3.8	9.3
crotonaldehyde	67.2	49.7	61.4	23.6	50.5
methacrolein	5.8	15.3	17.8	8.8	17.0
trans-2-hexenal	15.0	18.2	27.0	50.4	39.7
trans-2-decenal	1.2	4.8	7.5	5.0	4.7
methyl vinyl ketone	49.1	39.8	54.1	35.4	43.4
<u>Hydroxycarbonyls</u>					
hydroxyacetaldehyde	107	63.3	22.1	28.3	52.0
hydroxyacetone	122	114	89.9	71.9	76.6

Table C.1. Results of the Carbonyl Analysis for the Fireplace Combustion of Selected Woods (all values in milligram compound per kilogram wood burned)

Compound	Red Maple	Sugar Maple	Douglas Fir	Loblolly Pine	White Oak
1-hydroxy-2-butanone	52.7	38.3	24.8	16.5	19.2
Aromatics					
benzaldehyde	25.1	12.1	25.9	42.1	28.5
acetophenone	35.6	20.5	19.3	23.3	7.8
o-tolualdehyde	18.1	14.7	11.8	16.2	7.4
m-tolualdehyde	15.3	13.8	22.8	61.3	36.6
p-tolualdehyde	22.7	20.3	41.0	36.5	43.8
2,5-dimethylbenzaldehyde	16.9	20.5	21.3	19.4	16.4
(m+p)-anisaldehyde	18.1	13.2	16.2	8.5	10.5
vanillin	38.3	34.4	59.8	43.0	37.1
t-cinnamaldehyde	10.4	6.3	3.1	0.9	5.0
Dicarbonyls					
glyoxal	361	848	563	525	830
methylglyoxal	387	673	464	470	1042
2-oxobutanal	335	382	121	148	935
biacetyl	203	401	217	169	498
succinnic dialdehyde	41.7	41.9	19.3	26.2	46.6
3-oxobutanal	1.8	3.5	4.6	10.6	10.6
2,3-pentanedione	44.8	93.6	57.2	36.5	138
glutaraldehyde	37.4	38.7	27.0	21.5	35.7
2-oxohexanal	8.9	7.8	6.6	7.7	8.1
3,4-hexanedione	30.1	42.0	55.5	40.4	53.9
Furan Carbonyls					
2-furaldehyde	118	93.9	60.0	18.3	76.2
5-methyl-2-furaldehyde	78.2	66.2	57.7	72.8	55.4
2-acetyl-furan	13.2	13.4	4.2	12.7	14.8

Table C.1. Results of the Carbonyl Analysis for the Fireplace Combustion of Selected Woods (all values in milligram compound per kilogram wood burned)

Compound	Red Maple	Sugar Maple	Douglas Fir	Loblolly Pine	White Oak
5-hydroxy-2-methyl-furaldehyde	38.3	25.3	29.1	13.3	27.5
<u>Keto Acids</u>					
glyoxylic acid	3.7	1.7	2.0	0.3	2.1
pyruvic acid	26.7	27.0	26.8	11.8	17.7
<u>Tentatively identified compounds (a)</u>					
3-penten-2-one	13.8	12.1	8.5	3.8	13.1
2-hydroxybenzaldehyde	8.9	6.0	4.4	4.7	4.0
indanone	6.1	6.1	7.2	5.0	6.9
acetovanillone	14.1	11.7	20.6	12.7	12.7
coniferyl aldehyde	8.0	6.5	23.0	30.3	6.8
syringaldehyde	15.6	16.0	nd	nd	15.2
acetosyringone	5.8	3.0	nd	nd	6.3
sinapinic aldehyde	9.8	7.8	nd	nd	7.8
2-ketobutyric acid	6.7	3.0	6.4	12.4	10.0
1,4-benzoquinone	3.4	2.4	1.5	1.8	3.5
5-hydroxy-2-pentanone	5.5	3.9	2.2	2.4	5.3
<u>Tentatively identified compounds (b)</u>					
o-anisaldehyde	18.1	16.4	27.0	25.9	13.1

nd = not detected

(a) Tr, UV and Mass Spectra match that of standard but coelute with another compound.

(b) Tr, UV and Mass Spectra match that of standard for an isomer.

Table C.2. Results of the Carbonyl Analysis for the Wood Stove Combustion of Selected Woods (all values in milligram compound per kilogram wood burned)

Compound	White Oak		Red Maple		Sugar Maple		Douglas Fir		Loblolly Pine	
	Non-catalyst	Catalyst	Non-catalyst	Catalyst	Non-catalyst	Catalyst	Non-catalyst	Catalyst	Non-catalyst	Catalyst
<u>Aldehydes</u>										
formaldehyde	358	360	159		198		181	175	298	
acetaldehyde	327	327	106		173		144	185	274	
propanal	57.5	41.9	9.8		17.3		12.0	17.2	33.4	
butanal and / or isobutanal	11.5	13.1	6.8		7.0		5.7	5.1	4.8	
isopentanal	29.0	22.4	4.5		5.6		8.7	9.4	27.0	
pentanal	7.2	7.3	1.8		2.1		3.4	4.7	11.8	
hexanal	2.6	2.5	0.9		1.0		2.2	2.1	3.8	
heptanal	0.3	0.6	0.4		1.0		1.9	1.4	2.7	
octanal	0.6	0.7	0.5		0.7		1.3	0.7	1.8	
nonanal	1.4	1.3	1.2		1.4		1.3	1.2	2.2	
decanal	3.8	4.0	2.7		2.6		1.0	1.0	1.9	
<u>Ketones</u>										
acetone	177	147	43.3		66.2		61.8	78.9	112	
2-butanone	26.0	19.6	8.9		9.2		7.4	11.6	14.0	
<u>Unsaturated Carbonyls</u>										
acrolein	4.4	2.2	0.2		0.3		1.0	0.2	1.2	
crotonaldehyde	15.2	7.4	3.1		3.1		2.0	1.6	6.4	
methacrolein	6.5	2.0	0.3		0.4		0.4	0.5	0.6	
trans-2-hexenal	2.3	2.2	1.1		0.8		0.6	0.5	1.5	
trans-2-decenal	2.0	1.0	1.0		1.1		0.8	0.2	0.7	
methyl vinyl ketone	6.6	3.2	1.3		1.4		0.9	0.7	2.7	
<u>Hydroxycarbonyls</u>										
hydroxyacetaldehyde	25.0	18.2	5.9		5.4		3.4	3.2	3.5	
hydroxyacetone	41.7	26.1	13.7		20.2		15.0	10.1	33.6	
1-hydroxy-2-butanone	16.4	7.1	5.3		8.3		4.7	2.5	10.3	

Table C.2. Results of the Carbonyl Analysis for the Wood Stove Combustion of Selected Woods (all values in milligram compound per kilogram wood burned)

Compound	White Oak		Red Maple		Sugar Maple		Douglas Fir		Loblolly Pine	
	Non-catalyst	Catalyst	Non-catalyst	Catalyst	Non-catalyst	Catalyst	Non-catalyst	Catalyst	Non-catalyst	Catalyst
Aromatics										
benzaldehyde	14.2	20.9	6.6		7.3		11.3	17.2	14.0	
acetophenone	19.4	18.9	11.0		8.9		9.0	6.2	10.9	
o-tolualdehyde	4.1	2.4	1.2		1.9		2.6	3.2	4.8	
m-tolualdehyde	15.6	17.0	15.2		9.5		6.5	11.9	16.7	
p-tolualdehyde	19.4	26.0	24.3		12.7		9.0	15.9	19.9	
2,5-dimethylbenzaldehyde	3.1	7.5	6.5		10.9		3.6	3.2	17.0	
(m+p)-anisaldehyde	3.2	1.9	0.6		0.6		1.5	0.8	2.6	
vanillin	10.1	15.3	4.0		7.6		5.3	3.9	7.4	
t-cinnamaldehyde	5.4	4.6	1.8		2.7		2.5	0.9	1.5	
Dicarbonyls										
glyoxal	279	234	169		268		238	180	431	
methylglyoxal	279	249	134		218		143	146	411	
2-oxobutanal	320	225	125		97.5		56.0	51.7	153	
biacetyl	273	227	89.9		129		85.9	99.2	225	
succinnic dialdehyde	13.5	9.1	5.7		4.9		2.6	1.8	5.7	
3-oxobutanal	3.1	1.0	1.0		0.2		1.7	1.0	1.8	
2,3-pentanedione	57.4	65.9	18.0		23.4		17.2	25.7	59.3	
glutaraldehyde	10.7	10.0	5.0		3.8		4.6	2.7	4.0	
2-oxohexanal	7.2	5.7	1.7		5.0		1.9	1.1	3.0	
3,4-hexanedione	10.7	10.0	4.0		3.0		4.4	5.0	6.3	
Furan Carbonyls										
2-furaldehyde	32.5	9.6	7.5		6.6		6.7	4.2	7.1	
5-methyl-2-furaldehyde	24.9	6.6	6.1		3.8		7.0	3.9	14.4	
2-acetylfuran	7.5	2.8	2.0		1.0		0.8	8.1	2.5	
5-hydroxy-2-methyl-furaldehyde	13.8	7.3	2.5		2.8		3.6	1.5	3.4	
Keto Acids										
glyoxylic acid	1.7	1.0	0.3		0.5		0.6	0.3	1.5	

Table C.2. Results of the Carbonyl Analysis for the Wood Stove Combustion of Selected Woods (all values in milligram compound per kilogram wood burned)

Compound	White Oak		Red Maple		Sugar Maple		Douglas Fir		Loblolly Pine	
	Non-catalyst	Catalyst	Non-catalyst	Catalyst	Non-catalyst	Catalyst	Non-catalyst	Catalyst	Non-catalyst	Catalyst
pyruvic acid	6.7	4.2	1.0	1.0	3.3	2.5	1.9	4.0		
<u>Tentatively identified compounds (a)</u>										
3-penten-2-one	7.5	4.6	3.9	3.3	3.3	3.6	1.4	3.5		
2-hydroxybenzaldehyde	6.3	6.4	3.3	2.4	3.4	4.2	4.3	7.6		
indanone	3.8	7.4	2.4	3.6	1.9	2.8	2.7	2.0		
acetovanillone	9.9	7.2	1.5	1.3	5.0	1.3	0.8	1.8		
coniferyl aldehyde	4.9	2.9	3.8	5.2	2.4	0.08	0.8	3.6		
syringaldehyde	12.0	5.2	0.9	3.7	5.2	0.05	0.04	0.05		
acetosyringone	3.9	3.1	1.4	0.9	0.9	0.07	0.04	0.02		
sinapinic aldehyde	4.3	0.9	0.4	3.1	2.3	0.8	0.02	0.08		
2-ketobutyric acid	1.3	1.4	0.7	0.4	0.3	0.4	0.5	1.8		
1,4-benzoquinone	1.3	1.2	0.3	0.7	0.5	0.4	0.1	0.9		
5-hydroxy-2-pentanone	1.6				0.7	0.3	0.2	0.7		
<u>Tentatively identified compounds (b)</u>										
o-anisaldehyde	3.7	2.4	0.4	0.4	0.4	1.7	0.5	1.5		

(a) Tr, UV and Mass Spectra match that of standard but coelute with another compound.

(b) Tr, UV and Mass Spectra match that of standard for an isomer.

Appendix D

Description of Procedures for GC/MS Identification and Quantification

Individual organic compounds presented in this work were identified and quantified based on methods previously developed by the Cass research group. The laboratory procedures for spiking, extraction, concentration, splitting, derivatization, and injection are described in the main chapters of the thesis. The following discussion provides an outline of the identification techniques and quantification calculations that were utilized subsequent to a successful GC/MS run.

The first step in identifying individual compounds is to look at the mass to charge (m/z) spectrum for every distinguishable peak in the total ion chromatogram (TIC) (Figure D.1). Background subtraction is used to refine the mass spectrum and help distinguish between peaks that overlap or co-elute. A library search based on the mass spectrum performed by the HP data analysis software yields potential matches for most of the peaks. The retention time and tentative identification of each peak is recorded. When no good match is found, the peak's retention time is recorded and identified as unknown.

Confirmation of the tentative identifications of the peaks is done by comparison with the retention times and mass spectra of known standard compounds injected onto the GC/MS in separate runs (Figure D.2). Often, when a matching standard compound is not available, identification is based on the retention time of the peak compared to other compounds in the same homologous series with similar mass spectra. For example, C_{21} alkane will elute approximately halfway between C_{20} alkane and C_{22} alkane, and have the

same distinctive alkane mass spectra (Figure D.3). The existence of parent ions in the mass spectra (corresponding to the molecular weight of the compound) further confirms the identification of such homologues. For some of the remaining tentatively identified and unknown peaks, for which no exact or homologous standard is available, identification can be confirmed based on interpretation of the fragmentation patterns seen in the mass spectra and relative retention times. Prior knowledge of and experience with the types of compounds expected in the samples are also important tools in identifying individual compounds based on mass spectral interpretation.

Once as many of the initially identified peaks are assigned to individual organic compounds as possible, additional effort is made to find other compounds for which a peak was not evident in the total ion chromatogram. For every compound for which a standard is available, individual ions associated with that compound are extracted and the presence of a peak for these ions at the proper retention time is assessed. The positive identification of some organic compounds often suggest the presence of homologous or similar compounds; the presence of such compounds is also assessed using the appropriate extracted individual ion chromatograms.

The quantification of the positively identified peaks is based on a large set of authentic standard suites run separately but on the same day of the sample runs. Approximately 12 standard mixtures containing over one hundred individual organic compounds of known concentrations have been created. An additional mixture of deuterated compounds (Figure D.1), spanning different retention times and polarities, is used to spike the filters prior to extraction in order to determine recovery efficiencies. Finally, a co-injection standard of 1-phenyldodecane (1-PD) is separately entrained into

the injection needle containing the sample prior to manual injection (Figure D.1).

Volumes of both 1-PD and the sample, separated by an air pocket, are manually read from the graduated needle. The 1-PD co-injection is meant to track overall instrument response.

Relative response factors (RRFs) for each compound in the standard suites are based on peak areas of selected ions. Between one and three ions for each compound are selected for their high relative abundance and their relative uniqueness to nearby compounds and background noise. The software extracts the ions of interest from the total ion chromatogram enabling the manual integration of each ion peak (Figure D.3). The areas of the peaks of each ion are summed to yield a final total area. All RRFs are calculated relative to the total ion area response of the 1-PD co-injection standard. The mass of each standard compound injected is known from the volume of sample injected and the known concentration of the compound in the standard suite. Thus, RRFs for each standard compound are calculated as follows:

$$\text{RRF} = \frac{\left(\frac{\text{mass of standard compound injected}}{\text{mass of 1-PD injected}} \right)}{\left(\frac{\text{sum of peak areas of selected ions of standard compound}}{\text{TIC area of 1-PD}} \right)}$$

RRFs are thus assigned to all compounds for which standards are available. For all other compounds for which quantification is desired, RRFs are assigned based on the compound's similarity to available standard compounds. Compounds with similar fragmentation patterns and nearby retention times, which, for example, may only differ from a standard compound by an extra carbon group, are assigned the same RRF as the

standard. For homologous series for which several standards within the series are available, RRFs are interpolated or extrapolated from a best fit curve to a RRF vs. retention time plot. Finally, if no homologous standards or standards with analogous fragmentation exist for a given compound, the total ion area response of a standard with similar polarity and retention time is assumed to be equivalent to the total ion response of that compound. Thus, a new RRF is calculated based on the ratio of the summed selected ion areas to the total ion areas.

Once RRFs for every compound of interest are assigned, the actual mass of each compound in each injected sample can be calculated according to the equation

mass of compound injected =

$$(\text{RRF}) (\text{mass of 1-PD injected}) \left(\frac{\text{sum of peak areas of selected ions of compound}}{\text{TIC area of 1-PD}} \right)$$

where the RRF is the response factor for that particular compound. The mass of 1-PD is based on the known concentration of 1-PD in the co-injection solution and the volume of that solution read from the needle prior to injection. The mass of the compound injected can easily be converted to the mass of the compound in the total extract by multiplying by the ratio of the final extract volume to the injected sample volume. Then, these values are adjusted for the split volumes described below to get the mass of each compound in the extract prior to the split.

Extraction recoveries for each individual organic compound are based on the quantification of the deuterated compounds in the spike solution. RRFs for these

compounds are based on separate GC/MS runs of the deuterated spike solution, and quantification is performed the same way as all other compounds. The mass of the spiked compounds added to the sample is known from the initial spike volume and spike solution concentrations. Thus the spiked mass is compared to the final measured mass to determine a recovery efficiency for each of the deuterated compounds in the spike. The spike solution used here consists of several deuterated alkanes, PAH, and alkanolic acids and a recovery curve, based on retention time, is constructed from the recovery efficiencies of these compounds. A best-fit straight line through a plot of the four deuterated PAH recovery efficiencies vs. retention time is used to estimate recoveries of all other compounds with retention times greater than 20 minutes. A best-fit line from the lightest deuterated alkane recovery efficiency to the 20 minute value of the deuterated PAH line is used to estimate recovery efficiencies for all compounds with retention times less than 20 minutes. Once recovery efficiencies for all the quantified compounds are known, the results for the mass of each compound in the extracted sample is divided by the recovery efficiency to yield the total mass of each compound on the filter prior to extraction, the desired result of the quantification procedure.

During the volume reduction step of the extraction procedure, when the sample volume is approximately 1 ml, the sample is split into two fractions. One remains a neutral fraction and is further reduced in volume while the second is derivatized with diazomethane prior to further volume reduction. The derivatization converts organic acids in the sample to their less polar methyl ester analogues which are more amenable to GC/MS analysis. Quantification results for all of the straight chain acids, resin acids, and benzoic acids were based on the derivatized sample fraction. Quantification procedures

are identical to those used for the neutral sample fraction, except that the deuterated alkanolic acids in the spike were used to estimate the combination of recovery and derivatization efficiencies. For methylated acids with retention times less than 25 minutes, a best-fit line to a plot of the three deuterated alkanolic acid recovery efficiencies vs. retention time was used. Methylated acids with retention times greater than 25 minutes were assigned a recovery equal to the 25 minute value of the aforementioned best-fit line.

Throughout the sample volume reduction process, sample volumes are measured and recorded. The volume in each of the split fractions, and the total final volume of each extract prior to injection are both important parameters in the subsequent quantification calculation.

The quantification procedures outlined above were used to quantify all the organic compounds in the smokes from the fireplace and wood stove source tests. However, a slightly modified approach was employed for the foliar and agricultural tests (Chapter 6) and the ambient samples (Chapter 8). Rather than manual injection, an auto-injection system was utilized. Furthermore, an increased number of isotopically-labeled (IL) compounds in a new spike solution were added to all of the authentic standard mixtures. A new RRF* is then calculated relative to an appropriate standard IL reference compound, rather than the now eliminated co-injection of 1-PD:

$$\text{RRF}^* = \frac{\left(\frac{\text{mass of standard compound injected}}{\text{mass of IL reference compound injected}} \right)}{\left(\frac{\text{sum of peak areas of selected ions of standard compound}}{\text{sum of peak areas of selected ions of IL ref. compound}} \right)}$$

When the samples are run, these RRFs are applied in a similar manner as that outlined above:

$$\begin{aligned} &\text{mass of compound on filter prior to extraction} = \\ &(\text{RRF}^*) \times (\text{mass of IL ref. compound spiked onto filter}) \\ &\times \left(\frac{\text{sum of peak areas of selected ions of compound}}{\text{sum of peak areas of selected ions of IL ref. compound}} \right) \end{aligned}$$

In the new calculation, all recoveries, instrument responses, derivatization efficiencies, and volume splits are already accounted for. The new spike solution includes more compounds than the alkanes, PAH, and alkanoic acids of the previous spike solution. Among these is a C₁₃-labeled levoglucosan which greatly improves the accuracy of levoglucosan quantification. Each organic compound for which quantification is performed requires an appropriate IL reference compound by which the RRF* is calculated. Obviously, if the organic compound to be quantified has an exact IL analogue in the spike solution, that IL compound is used. For other compounds, the IL reference compound is chosen which best approximates the given compound's polarity and retention time.

Figure D.1. Total ion chromatogram for fireplace white oak combustion with selected labeled peaks

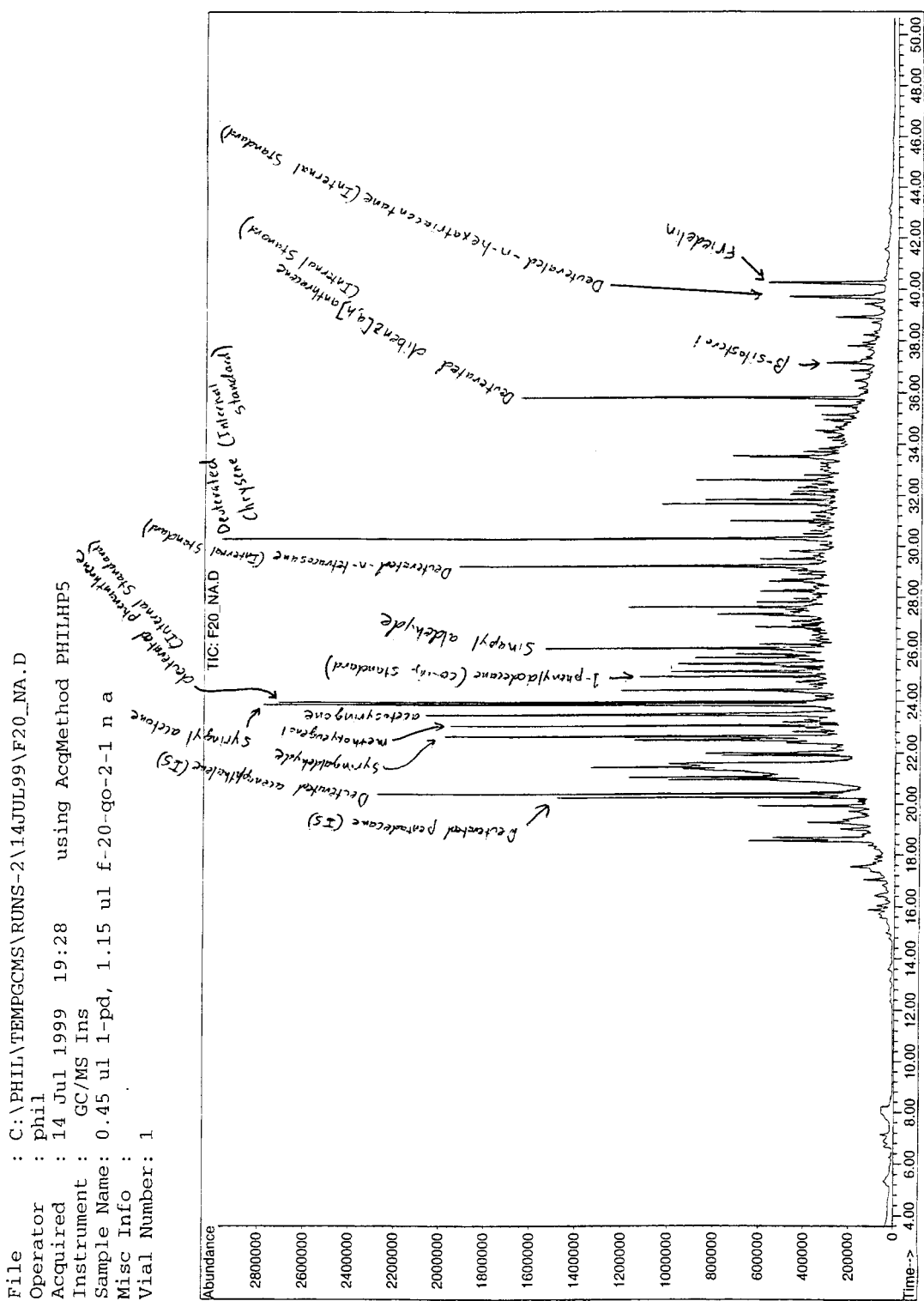


Figure D.2. Total ion chromatogram for authentic standard np-1 with selected labeled peaks

File : C:\PHIL\TEMPGMS\RUNS-2\14JUL99\NP1_A.D
 Operator : phil
 Acquired : 14 Jul 1999 12:38 using AcqMethod PHILHP5
 Instrument : GC/MS Ins
 Sample Name: 0.55 ul 1-pd, 1.05 ul np1 1:1 a
 Misc Info :
 Vial Number: 1

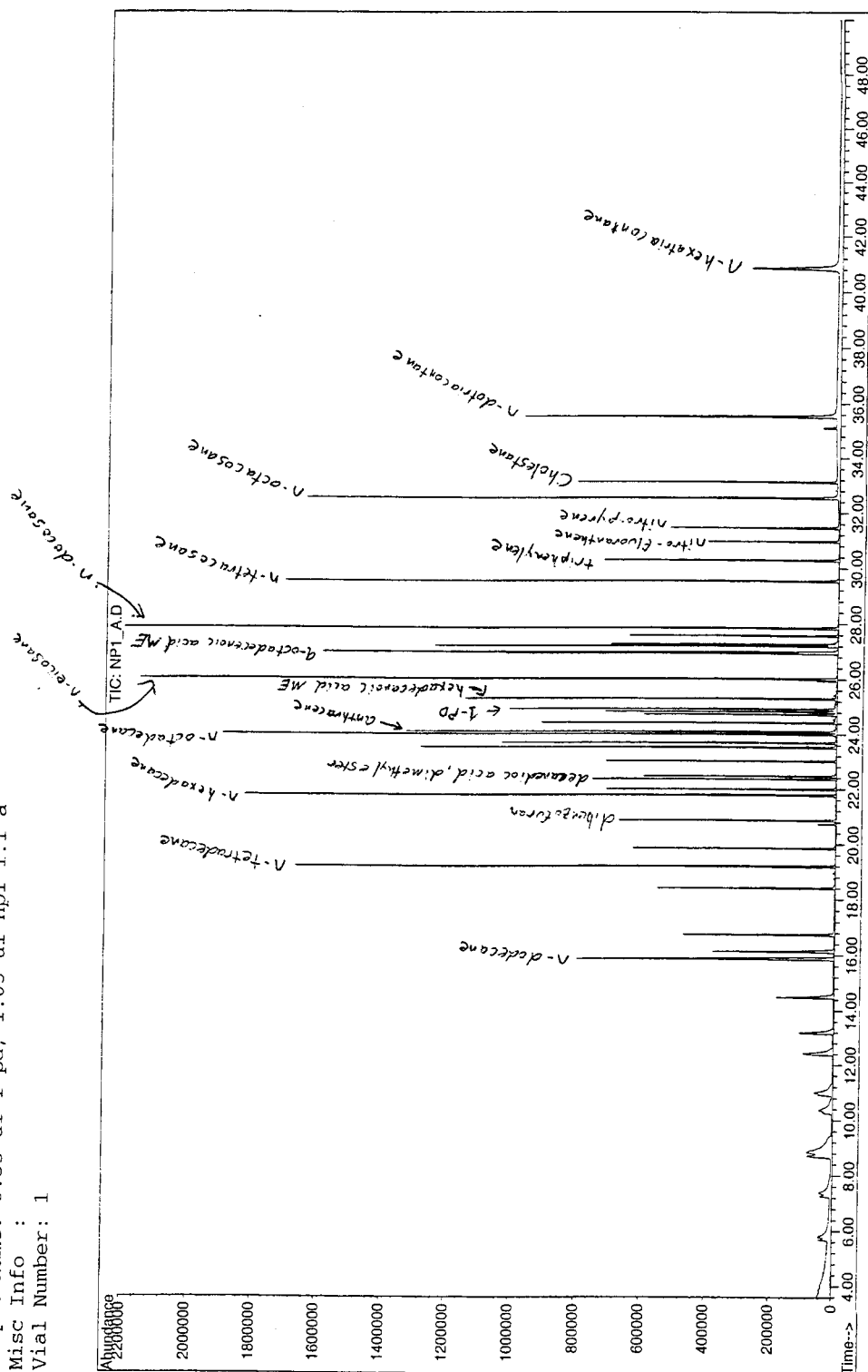


Figure D.3. Extracted ion chromatogram and mass spectra demonstrating n-heneicosane identification using homologous compounds

File : C:\PHIL\TEMPGCMS\RUNS-2\14JUL99\F20_NA.D
 Operator : phil
 Acquired : 14 Jul 1999 19:28 using AcqMethod PHILHP5
 Instrument : GC/MS Ins
 Sample Name: 0.45 ul 1-pd, 1.15 ul f-20-qo-2-1 n a
 Misc Info :
 Vial Number: 1

